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Dated 8 October 2003

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# Patents Form 1/77

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**The Patent Office**
Cardiff Road
Newport
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## Request for grant of a patent

1. Your Reference — RWF/MJM/X957

2. Application number — 0309812.6 — 30 APR 2003

3. Full name, address and postcode of the or each Applicant

   Country/state of incorporation (if applicable)

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   8432809001

   **Incorporated in: United Kingdom**

4. Title of the invention — **METALLOCENE CATALYST**

5. Name of agent — **APPLEYARD LEES**

   Address for service in the UK to which all correspondence should be sent

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   **HALIFAX**
   **HX1 2HY**

   Patents ADP number — **190001**

6. Priority claimed to:

| Country | Application number | Date of filing |
|---|---|---|
| | | |

7. Divisional status claimed from:

| Number of parent application | Date of filing |
|---|---|
| - | - |

8. Is a statement of inventorship and of right to grant a patent required in support of this application? — **YES**

| | | |
|---|---|---|
| 9. | Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document | |
| | Continuation sheets of this form | - |
| | Description | 80 |
| | Claim(s) | 12 |
| | Abstract | 1 |
| | Drawing(s) | - |
| 10. | If you are also filing any of the following, state how many against each item | |
| | Priority documents | - |
| | Translation of priority documents | - |
| | Statement of inventorship and right to grant a patent (PF 7/77) | - |
| | Request for a preliminary examination and search (PF 9/77) | - |
| | Request for substantive examination (PF 10/77) | - |
| | Any other documents (please specify) | - |

11. We request the grant of a patent on the basis of this application.

Signature — Date

**APPLEYARD LEES** — **29 April 2003**

Appleyard Lees.

12. Contact — **Richard W Frith- 01422 330110**

# METALLOCENE CATALYST

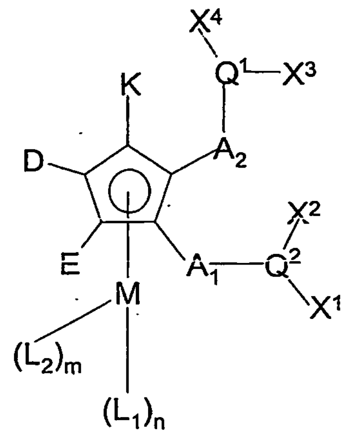
The present invention relates to compounds, in particular compounds for catalysing the carbonylation of ethylenically unsaturated compounds, methods of preparing such compounds and the use of such compounds for catalysing the carbonylation of ethylenically unsaturated compounds.

The carbonylation of ethylenically unsaturated compounds using carbon monoxide in the presence of a catalyst system and an alcohol or water to yield the corresponding ester or carboxylic acid, respectively, is well known. Suitable catalyst systems comprise a Group VIII metal (e.g. palladium) and a phosphine ligand (e.g. an alkyl phosphine or a bidentate phosphine ligand as disclosed in WO-A-9619434).

Although catalyst systems have been developed which exhibit reasonable stability during the carbonylation process and permit relatively high reaction rates to be achieved, there still exists a need for improved catalyst systems. Suitably, the present invention aims to provide an improved catalyst for carbonylating ethylenically unsaturated compounds.

According to a first aspect, the present invention provides a catalyst suitable for carbonylating an ethylenically unsaturated compound, which catalyst is obtainable by combining:

(a) a Group VIIIB metal or a compound thereof; and,
(b) a compound of formula I or salt thereof:




(I)

wherein:

$A_1$ and $A_2$, and $A_3$, $A_4$ and $A_5$ (when present), each independently represent lower alkylene;

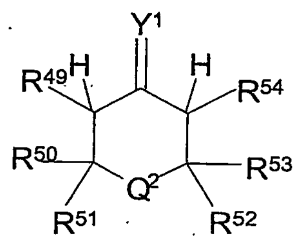
K is selected from the group consisting of hydrogen, lower alkyl, aryl, Het, halo, cyano, nitro, $-OR^{19}$, $-OC(O)R^{20}$, $-C(O)R^{21}$, $-C(O)OR^{22}$, $-N(R^{23})R^{24}$, $-C(O)N(R^{25})R^{26}$, $-C(S)(R^{27})R^{28}$, $-SR^{29}$, $-C(O)SR^{30}$, $-CF_3$ or $-A_3-Q^3(X^5)X^6$;

D is selected from the group consisting of hydrogen, lower alkyl, aryl, Het, halo, cyano, nitro, $-OR^{19}$, $-OC(O)R^{20}$, $-C(O)R^{21}$, $-C(O)OR^{22}$, $-N(R^{23})R^{24}$, $-C(O)N(R^{25})R^{26}$, $-C(S)(R^{27})R^{28}$, $-SR^{29}$, $-C(O)SR^{30}$, $-CF_3$ or $-A_4-Q^4(X^7)X^8$;

E is selected from the group consisting of hydrogen, lower alkyl, aryl, Het, halo, cyano, nitro, $-OR^{19}$, $-OC(O)R^{20}$, $-C(O)R^{21}$, $-C(O)OR^{22}$, $-N(R^{23})R^{24}$, $-C(O)N(R^{25})R^{26}$, $-C(S)(R^{27})R^{28}$, $-SR^{29}$, $-C(O)SR^{30}$, $-CF_3$ or $-A_5-Q^5(X^9)X^{10}$;

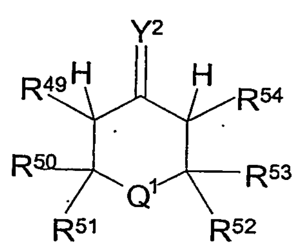
or both D and E together with the carbon atoms of the cyclopentadienyl ring to which they are attached form an optionally substituted phenyl ring:

$X^1$ represents $CR^1(R^2)(R^3)$ or adamantyl, $X^2$ represents $CR^4(R^5)(R^6)$ or adamantyl, or $X^1$ and $X^2$ together with $Q^2$ to which they are attached form an optionally substituted 2-phospha-tricyclo[3.3.1.1{3,7}]decyl group or derivative thereof, or $X^1$ and $X^2$ together with $Q^2$ to which they are attached form a ring system of formula 1a



(1a)

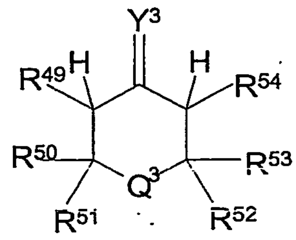
$X^3$ represents $CR^7(R^8)(R^9)$ or adamantyl, $X^4$ represents $CR^{10}(R^{11})(R^{12})$ or adamantyl, or $X^3$ and $X^4$ together with $Q^1$ to which they are attached form an optionally substituted 2-phospha-tricyclo[3.3.1.1{3,7}]decyl group or derivative thereof, or $X^3$ and $X^4$ together with $Q^1$ to which they are attached form a ring system of formula 1b



(1b)

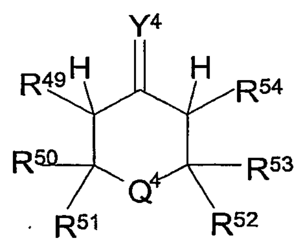
$X^5$ represents $CR^{13}(R^{14})(R^{15})$ or adamantyl, $X^6$ represents $CR^{16}(R^{17})(R^{18})$ or adamantyl, or $X^5$ and $X^6$ together with $Q^3$ to which they are attached form an optionally substituted 2-phospha-tricyclo[3.3.1.1{3,7}]decyl group or derivative

thereof, or $X^5$ and $X^6$ together with $Q^3$ to which they are attached form a ring system of formula 1c



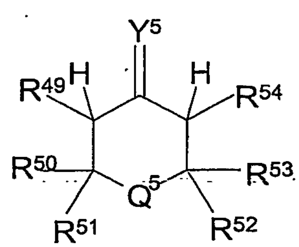
(1c)

$X^7$ represents $CR^{31}(R^{32})(R^{33})$ or adamantyl, $X^8$ represents $CR^{34}(R^{35})(R^{36})$ or adamantyl, or $X^7$ and $X^8$ together with $Q^4$ to which they are attached form an optionally substituted 2-phospha-tricyclo[3.3.1.1{3,7}]decyl group or derivative thereof, or $X^7$ and $X^8$ together with $Q^4$ to which they are attached form a ring system of formula 1d



(1d)

$X^9$ represents $CR^{37}(R^{38})(R^{39})$ or adamantyl, $X^{10}$ represents $CR^{40}(R^{41})(R^{42})$ or adamantyl, or $X^9$ and $X^{10}$ together with $Q^5$ to which they are attached form an optionally substituted 2-phospha-tricyclo[3.3.1.1.{3,7}]decyl group or derivative thereof, or $X^9$ and $X^{10}$ together with $Q^5$ to which they are attached form a ring system of formula 1e



(1e)

$Q^1$ and $Q^2$, and $Q^3$, $Q^4$ and $Q^5$ (when present), each independently represent phosphorus, arsenic or antimony;

M represents a Group VIB or VIIIB metal or metal cation thereof;

$L_1$ represents an optionally substituted cyclopentadienyl, indenyl or aryl group;

$L_2$ represents one or more ligands each of which are independently selected from hydrogen, lower alkyl, alkylaryl, halo, CO, $P(R^{43})(R^{44})R^{45}$ or $N(R^{46})(R^{47})R^{48}$;

$R^1$ to $R^{18}$ and $R^{31}$ to $R^{42}$, when present, each independently represent lower alkyl, aryl, halo or Het;

$R^{19}$ to $R^{30}$ and $R^{43}$ to $R^{48}$, when present, each independently represent hydrogen, lower alkyl, aryl or Het;

$R^{49}$, $R^{54}$ and $R^{55}$, when present, each independently represent hydrogen, lower alkyl or aryl;

$R^{50}$ to $R^{53}$, when present, each independently represent lower alkyl, aryl or Het;

$Y^1$, $Y^2$, $Y^3$, $Y^4$ and $Y^5$, when present, each independently represent oxygen, sulfur or $N\text{-}R^{55}$;

$n = 0$ or $1$;

and $m = 0$ to $5$;

provided that when n = 1 then m equals 0, and when n equals 0 then m does not equal 0;

provided that when both K represents $-A_3-Q^3(X^5)X^6$ and E represents $-A_5-Q^5(X^9)X^{10}$, then D represents $-A_4-Q^4(X^7)X^8$.

Such compounds are referred to hereinafter as "the compounds of the invention".

Suitably, the compounds of the invention may catalyse the carbonylation of unsaturated compounds, particularly ethylenically unsaturated compounds, in the presence of carbon monoxide and a coreactant. In particular, the compounds of the invention may be employed in hydroformylation reactions, hydrocarboxylation reactions, hydroesterification reactions and hydroamidation reactions.

Suitably, the compounds of the invention may catalyse the carbonylation of an ethylenically unsaturated compound in the presence of carbon monoxide and a hydroxyl group containing compound i.e. the compounds of the invention may catalyse the conversion of an ethylenically unsaturated compound to the corresponding carboxylic acid or ester, respectively, depending on the choice of hydroxyl group containing compound used. Conveniently, the compounds of the invention may exhibit a high stability under typical carbonylation reaction conditions such that they require little or no replenishment. Conveniently, the compounds of the invention may increase the rate of the carbonylation reaction of an ethylenically unsaturated compound compared to known catalysts. Conveniently, the compounds of the invention may promote high conversion

rates of the ethylenically unsaturated compound, thereby yielding the desired product in high yield with little or no impurities. Consequently, employing the compounds of the invention may increase the commercial viability of a carbonylation process, such as the carbonylation of an ethylenically unsaturated compound.

Suitably, the compounds of the invention typically exhibit a high catalytic turnover in the carbonylation of an unsaturated compound, particularly an ethylenically unsaturated compound, in the presence of carbon monoxide and a co-reactant as defined herein. It will be appreciated by those skilled in the art that in the compounds of the invention each of $Q^1$ and $Q^2$, are bonded to a tertiary carbon atom present in both $X^3$ and $X^4$, and both $X^1$ and $X^2$ respectively. Similarly each of $Q^3$, $Q^4$ and $Q^5$ when present are bonded to a tertiary carbon atom present in both $X^5$ and $X^6$, and both $X^7$ and $X^8$, and both $X^9$ and $X^{10}$, respectively. Unexpectedly, it has been found that if each of $Q^1$, $Q^2$, $Q^3$, $Q^4$ and $Q^5$, respectively, is bonded to two tertiary carbon atoms, then this typically produces an increased catalytic turnover in the carbonylation of an unsaturated compound, compared with a comparable compound where any of $Q^1$, $Q^2$, $Q^3$, $Q^4$ and $Q^5$ is bonded to a secondary or primary carbon atom in $X^1$ to $X^{10}$, respectively, or bonded to a hydrogen atom.

The term "aryl" when used herein, includes six- to ten-membered carbocyclic aromatic groups, such as phenyl and naphthyl, which groups are optionally substituted with one or more substituents selected from aryl, lower alkyl (which alkyl group may itself be optionally substituted or terminated as defined below), Het, halo, cyano, nitro,

$-OR^{19}$, $-OC(O)R^{20}$, $-C(O)R^{21}$, $-C(O)OR^{22}$, $-N(R^{23})R^{24}$, $-C(O)N(R^{25})R^{26}$, $-SR^{29}$, $-C(O)SR^{30}$ or $-C(S)N(R^{27})R^{28}$ wherein $R^{19}$ to $R^{30}$ each independently represent hydrogen, aryl or lower alkyl (which alkyl group may itself be optionally substituted or terminated as defined below).

The term "Het", when used herein, includes four- to twelve-membered, preferably four- to ten-membered ring systems, which rings contain one or more heteroatoms selected from nitrogen, oxygen, sulfur and mixtures thereof, and which rings contain one or more double bonds or be non-aromatic, partly aromatic or wholly aromatic in character. The ring systems may be monocyclic, bicyclic or fused. Each "Het" group identified herein is optionally substituted by one or more substituents selected from halo, cyano, nitro, oxo, lower alkyl (which alkyl group may itself be optionally substituted or terminated as defined below) $-OR^{19}$, $-OC(O)R^{20}$, $-C(O)R^{21}$, $-C(O)OR^{22}$, $-N(R^{23})R^{24}$, $-C(O)N(R^{25})R^{26}$, $-SR^{29}$, $-C(O)SR^{30}$ or $-C(S)N(R^{27})R^{28}$ wherein $R^{19}$ to $R^{30}$ each independently represent hydrogen, aryl or lower alkyl (which alkyl group itself may be optionally substituted or terminated as defined below). The term "Het" thus includes groups such as optionally substituted azetidinyl, pyrrolidinyl, imidazolyl, indolyl, furanyl, oxazolyl, isoxazolyl, oxadiazolyl, thiazolyl, thiadiazolyl, triazolyl, oxatriazolyl, thiatriazolyl, pyridazinyl, morpholinyl, pyrimidinyl, pyrazinyl, quinolinyl, isoquinolinyl, piperidinyl, pyrazolyl and piperazinyl. Substitution at Het may be at a carbon atom of the Het ring or, where appropriate, at one or more of the heteroatoms.

"Het" groups may also be in the form of an N oxide.

The term adamantyl when used herein means an adamantyl group which may be bonded to $Q^1$, $Q^2$, $Q^3$, $Q^4$ and $Q^5$, respectively, in position 1 or 2. Tricyclo[3.3.1.1.{3,7}]decyl is the systematic name for an adamantyl group, suitably $Q^1$, $Q^2$, $Q^3$, $Q^4$ and $Q^5$, respectively, may be bonded to the 1 position or 2 position of one or two tricyclo[3.3.1.1.{3,7}]decyl groups.

The adamantyl group may optionally comprise, besides hydrogen atoms, one or more substituents selected from lower alkyl, $-OR^{19}$, $-OC(O)R^{20}$, halo, nitro, $-C(O)R^{21}$, $-C(O)OR^{22}$, cyano, aryl, $-N(R^{23})R^{24}$, $-C(O)N(R^{25})R^{26}$, $-C(S)(R^{27})R^{28}$, $-CF_3$, $-P(R^{56})R^{57}$, $-PO(R^{58})(R^{59})$, $-PO_3H_2$, $-PO(OR^{60})(OR^{61})$, or $-SO_3R^{62}$, wherein $R^{19}$, $R^{20}$, $R^{21}$, $R^{22}$, $R^{23}$, $R^{24}$, $R^{25}$, $R^{26}$, $R^{27}$, $R^{28}$, lower alkyl, cyano and aryl are as defined herein and $R^{56}$ to $R^{62}$ each independently represent hydrogen, lower alkyl, aryl or Het.

Suitably, when the adamantyl group is substituted with one or more substituents as defined above, highly preferred substituents include unsubstituted $C_1$ to $C_8$ alkyl, $-OR^{19}$, $-OC(O)R^{20}$, phenyl, $-C(O)OR^{22}$, fluoro, $-SO_3H$, $-N(R^{23})R^{24}$, $-P(R^{56})R^{57}$, $-C(O)N(R^{25})R^{26}$ and $-PO(R^{58})(R^{59})$, $-CF_3$, wherein $R^{19}$ represents hydrogen, unsubstituted $C_1$-$C_8$ alkyl or phenyl, $R^{20}$, $R^{22}$, $R^{23}$, $R^{24}$, $R^{25}$, $R^{26}$ each independently represent hydrogen or unsubstituted $C_1$-$C_8$ alkyl, $R^{56}$ to $R^{53}$, $R^{56}$ each independently represent unsubstituted $C_1$-$C_8$ alkyl or phenyl.

Suitably, the adamantyl group may comprise, besides hydrogen atoms, up to 10 substituents as defined above, preferably up to 5 substituents as defined above, more preferably up to 3 substituents as defined above. Suitably, when the adamantyl group comprises, besides hydrogen atoms, one or more substituents as defined herein, preferably each substituent is identical. Especially preferred substituents are unsubstituted $C_1$-$C_8$ alkyl, particularly methyl, and trifluoromethyl. A highly preferred adamantyl group comprises hydrogen atoms only i.e. the adamantyl group is not substituted.

By the term 2-phospha-tricyclo[3.3.1.1.{3,7}]decyl group we mean a 2-phospha-adamantyl group formed by the combination of $X^1$ and $X^2$ together with $Q^2$ to which they are attached, a 2-phospha-adamantyl group formed by the combination of $X^3$ and $X^4$ together with $Q^1$ to which they are attached, a 2-phospha-adamantyl group formed by the combination of $X^5$ and $X^6$ together with $Q^3$ to which they are attached, a 2-phospha-adamantyl group formed by the combination of $X^7$ and $X^8$ together with $Q^4$ to which they are attached and a 2-phospha-adamantyl group formed by the combination of $X^9$ and $X^{10}$ together with $Q^5$ to which they are attached, wherein $Q^1$, $Q^2$, $Q^3$, $Q^4$ and $Q^5$ is in the 2-position of the adamantyl group and each of $Q^1$, $Q^2$, $Q^3$, $Q^4$ and $Q^5$ represents phosphorus.

The 2-phospha-tricyclo[3.3.1.1.{3,7}]decyl group (referred to as 2-phospha-adamantyl group herein) may optionally comprise, beside hydrogen atoms, one or more substituents. Suitable substituents include those substituents as defined herein in respect of the adamantyl group. Highly preferred substituents include lower alkyl, particularly

unsubstituted $C_1$-$C_8$ alkyl, especially methyl, trifluoromethyl, $-OR^{19}$ wherein $R^{19}$ is defined herein, particularly unsubstituted $C_1$-$C_8$ alkyl or aryl, and 4-dodecylphenyl. When the 2-phospha-adamantyl group includes more than one substituent, preferably each substituent is identical.

Preferably, the 2-phospha-adamantyl group is substituted on one or more of the 1, 3, 5 or 7 positions with a substituent as defined herein. More preferably, the 2-phospha-adamantyl group is substituted on each of the 1, 3 and 5 positions. Most preferably, the 2-phospha-adamantyl group is substituted on each of the 1, 3, 5 and 7 positions. When the 2-phospha-adamantyl group includes more than 1 substituent preferably each substituent is identical, especially preferred substituents are unsubstituted $C_1$-$C_8$ alkyl, particularly methyl, and trifluoromethyl.

Preferably, the 2-phospha-adamantyl group includes additional heteroatoms, other than the 2-phosphorous atom, in the 2-phospha-adamantyl skeleton. Suitable heteroatoms include oxygen and sulphur atoms, especially oxygen atoms. More preferably, the 2-phospha-adamantyl group includes one or more heteroatoms in the 6, 9 and 10 positions. Even more preferably, the 2-phospha-adamantyl group includes a heteroatom in each of the 6, 9 and 10 positions. Most preferably, when the 2-phospha-adamantyl group includes two or more heteroatoms in the 2-phospha-adamantyl skeleton, each of the heteroatoms are identical. An especially preferred 2-phospha-adamantyl group, which may optionally be substituted with one or more substituents as

defined herein, includes an oxygen atom in the 6, 9 and 10 position of the 2-phospha-adamantyl skeleton.

Highly preferred 2-phospha-adamantyl groups as defined herein include 2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxadamantyl group, 2-phospha-1,3,5-trimethyl-6,9,10-trioxadamantyl group, 2-phospha-1,3,5,7-tetra(trifluoromethyl)-6,9,10-trioxadamantyl group, and 2-phospha-1,3,5-tri(trifluoromethyl)-6,9,10-trioxadamantyl group. Most preferably, the 2-phospha-adamantyl is selected from 2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxadamantyl group or 2-phospa-1,3,5,-trimethyl-6,9,10-trioxadamantyl group.

The term "lower alkyl" when used herein, means $C_1$ to $C_{10}$ alkyl and includes methyl, ethyl, propyl, butyl, pentyl, hexyl and heptyl groups. Unless otherwise specified, alkyl groups may, when there is a sufficient number of carbon atoms, be linear or branched, be saturated or unsaturated, be cyclic, acyclic or part cyclic/acyclic, and/or be substituted or terminated by one or more substituents selected from halo, cyano, nitro, $-OR^{19}$, $-OC(O)R^{20}$, $-C(O)R^{21}$, $-C(O)OR^{22}$, $-N(R^{23})R^{24}$, $-C(O)N(R^{25})R^{26}$, $-SR^{29}$, $-C(O)SR^{30}$, $-C(S)N(R^{27})R^{28}$, aryl or Het, wherein $R^{19}$ to $R^{30}$ each independently represent hydrogen, aryl or lower alkyl, and/or be interrupted by one or more oxygen or sulfur atoms, or by silano or dialkylsilicon groups.

Lower alkyl groups which $R^1$ to $R^{62}$, K, D, E and $L_2$ may represent and which aryl, Het and $L_1$ may be substituted, may, when there is a sufficient number of carbon atoms, be linear or branched, be saturated or unsaturated, be cyclic, acyclic or part cyclic/acyclic, and/or be

interrupted by one or more of oxygen or sulfur atoms, or by silano or dialkylsilicon groups, and/or be substituted by one or more substituents selected from halo, cyano, nitro, $-OR^{19}$, $-OC(O)R^{20}$, $-C(O)R^{21}$, $-C(O)OR^{22}$, $-N(R^{23})R^{24}$, $-C(O)N(R^{25})R^{26}$, $-SR^{29}$, $-C(O)SR^{30}$, $-C(S)N(R^{27})R^{28}$, aryl or Het wherein $R^{19}$ to $R^{30}$ each independently represent hydrogen, aryl or lower alkyl.

Similarly, the term "lower alkylene" which $A_1$ and $A_2$, and $A_3$, $A_4$ and $A_5$ (when present), represent in a compound of formula I, when used herein, includes $C_1$ to $C_{10}$ groups which can be bonded at two places on the group and is otherwise defined in the same way as "lower alkyl".

Suitably, when D and E together with the carbon atoms of the cyclopentadienyl ring to which they are attached form an optionally substituted phenyl ring, the metal M or cation thereof is attached to an indenyl ring system. Suitably, the phenyl ring part of the indenyl ring system is optionally substituted by one or more substituents selected from hydrogen, lower alkyl, halo, cyano, nitro, $OR^{19}$, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $N(R^{23})R^{24}$, $C(O)N(R^{25})R^{26}$, $C(S)(R^{27})R^{28}$, $SR^{29}$, $CF_3$ or $C(O)SR^{30}$, where $R^{19}$ to $R^{30}$ are as defined herein.

By the term "M represents a Group VIB or VIIIB metal" in a compound of formula I we include metals such as Cr, Mo, W, Fe, Co, Ni, Ru and Rh.

By the term "metal cation thereof" we mean that the Group VIB or VIIIB metal (M) in the compound of formula I as defined herein has a positive charge. Suitably, the metal cation may be in the form of a salt or may comprise weakly

coordinated anions derived from halo, nitric acid; sulphuric acid; lower alkanoic (up to $C_{12}$) acids such as acetic acid and propionic acid; sulphonic acids such as methane sulphonic acid, chlorosulphonic acid, fluorosulphonic acid, trifluoromethane sulphonic acid, benzene sulphonic acid, naphthalene sulphonic acid, toluene sulphonic acid, e.g. p-toluene sulphonic acid, t-butyl sulphonic acid, and 2-hydroxypropane sulphonic acid; sulphonated ion exchange resins; perhalic acid such as perchloric acid; perfluororated carboxylic acid such as trichloroacetic acid and trifluoroacetic acid; orthophosphoric acid; phosphonic acid such as benzene phosphonic acid; and acids derived from interactions between Lewis acids and Broensted acids. Other sources which may provide suitable anions include the tetraphenyl borate derivatives.

Preferably M represents a Group VIB or VIIIB metal. In other words the total electron count for the metal M is 18.

Halo groups, which $L_2$ may represent and with which the above-mentioned groups may be substituted or terminated, include fluoro, chloro, bromo and iodo.

Where a compound of the formula (I) contains an alkenyl group, cis (E) and trans (Z) isomerism may also occur. The present invention includes the individual stereoisomers of the compounds of formula (I) and, where appropriate, the individual tautomeric forms thereof, together with mixtures thereof. Separation of diastereoisomers or cis and trans isomers may be achieved by conventional techniques, e.g. by fractional crystallisation,

chromatography or H.P.L.C. of a stereoisomeric mixture of a compound of the formula (I) or a suitable salt or derivative thereof. An individual enantiomer of a compound of the formula (I) may also be prepared from a corresponding optically pure intermediate or by resolution, such as by H.P.L.C. of the corresponding racemate using a suitable chiral support or by fractional crystallisation of the diastereoisomeric salts formed by reaction of the corresponding racemate with a suitable optically active acid or base, as appropriate.

All stereoisomers are included within the scope of the invention.

Suitable Group VIIIB metals or a compound thereof which may be combined with a compound of formula I thereby forming the compounds of the invention include cobalt, nickel, palladium, rhodium and platinum. Preferably, the Group VIIIB metal is palladium or a compound thereof. Suitable compounds of such Group VIIIB metals include salts of such metals with, or compounds comprising weakly coordinated anions derived from, nitric acid; sulphuric acid; lower alkanoic (up to $C_{12}$) acids such as acetic acid and propionic acid; sulphonic acids such as methane sulphonic acid, chlorosulphonic acid, fluorosulphonic acid, trifluoromethane sulphonic acid, benzene sulphonic acid, naphthalene sulphonic acid, toluene sulphonic acid, e.g. p-toluene sulphonic acid, t-butyl sulphonic acid, and 2-hydroxypropane sulphonic acid; sulphonated ion exchange resins; perhalic acid such as perchloric acid; perfluororated carboxylic acid such as trichloroacetic acid and trifluoroacetic acid; orthophosphoric acid; phosphonic acid such as benzene phosphonic acid; and acids

derived from interactions between Lewis acids and Broensted acids. Other sources, which may provide suitable anions, include the tetraphenyl borate derivatives. Additionally, zero valent palladium with labile ligands e.g. tri(dibenzylideneacetone)dipalladium may be used. Preferably, zero valent Group VIIIB metals with labile ligands are employed.

Suitably, the compounds of the invention when employed to catalyse the carbonylation of ethylenically unsaturated compounds include a source of anions. Conveniently, the source of anions may be derived by combining a Group VIIIB compound thereof as described in the preceding paragraph with a compound of formula I. Alternatively, or additionally, a separate source of anions as mentioned above may be added to the compounds of the present invention. Preferably, the source of anions are derived from an acid having a pKa less than 4, more preferably a pKa less than 3, as measured at 18°C in an aqueous solution.

It will be appreciated by those skilled in the art that the compounds of formula I (referred to as (b) above) may function as ligands that coordinate with the Group VIIIB metal or compound thereof (referred to as (a) above) to form the compounds of the invention. Typically, the Group VIIIB metal or compound thereof (a) coordinates to the one or more phosphorus, arsenic and/or antimony atoms of the compound of formula I. It will be appreciated that the compounds of formula I may be referred to broadly as "metallocenes".

Suitably, when n = 1 and $L_1$ represents an optionally substituted cyclopentadienyl or indenyl group, the compounds of formula I may contain either two cyclopentadienyl rings, two indenyl rings or one indenyl and one cyclopentadienyl ring (each of which ring systems may optionally be substituted as described herein). Such compounds may be referred to as "sandwich compounds" as the metal M or metal cation thereof is sandwiched by the two ring systems. The respective cyclopentadienyl and/or indenyl ring systems may be substantially coplanar with respect to each other or they may be tilted with respect to each other (commonly referred to as bent metallocenes).

Alternatively, when n = 1 and $L_1$ represents aryl, the compounds of the invention may contain either one cyclopentadienyl or one indenyl ring (each of which ring systems may optionally be substituted as described herein) and one aryl ring which is optionally substituted as defined herein. Suitably, when n = 1 and $L_1$ represents aryl then the metal M of the compounds of formula I as defined herein is typically in the form of the metal cation.

In a particularly preferred embodiment of the present invention, in a compound of formula I, n = 1, $L_1$ is defined herein and m = 0.

Preferably, when n = 1 in the compound of formula I, $L_1$ represents cyclopentadienyl, indenyl or aryl ring each of which rings are optionally substituted by one or more substituents selected from hydrogen, lower alkyl, halo, cyano, nitro, $-OR^{19}$, $-OC(O)R^{20}$, $-C(O)R^{21}$, $-C(O)OR^{22}$, $-N(R^{23})R^{24}$, $-C(O)N(R^{25})R^{26}$, $-C(S)(R^{27})R^{28}$ $-SR^{29}$, $-C(O)SR^{30}$,

$-CF_3$ or ferrocenyl (by which we mean the cyclopentadienyl, indenyl or aryl ring which $L_1$ may represent is bonded directly to the cyclopentadienyl ring of the ferrocenyl group), wherein $R^{19}$ to $R^{30}$ is as defined herein. More preferably, if the cyclopentadienyl, indenyl or aryl ring which $L_1$ may represent is substituted it is preferably substituted with one or more substituents selected from unsubstituted $C_1$-$C_6$ alkyl, halo, cyano, $-OR^{19}$, $-OC(O)R^{20}$, $-C(O)R^{21}$, $-C(O)OR^{22}$, $-N(R^{23})R^{24}$ where $R^{19}$, $R^{20}$, $R^{21}$, $R^{22}$, $R^{23}$ and $R^{24}$ each independently represent hydrogen or $C_1$-$C_6$ alkyl. Even more preferably, the cyclopentadienyl, indenyl or aryl ring which $L_1$ may represent is substituted with one or more substituents selected from unsubstituted $C_1$-$C_6$ alkyl.

Preferably, when n = 1, $L_1$ represents cyclopentadienyl, indenyl, phenyl or napthyl optionally substituted as defined herein. Preferably, the cyclopentadienyl, indenyl, phenyl or napthyl groups are unsubstituted. More preferably, $L_1$ represents cyclopentadienyl, indenyl or phenyl, each of which rings are unsubstituted. Most preferably, $L_1$ represents unsubstituted cyclopentadienyl.

Suitably, when n = 0, the compounds of the invention contain only one cyclopentadienyl or indenyl ring (each of which ring systems may optionally be substituted as described herein). Such compounds may be referred to as "half sandwich compounds". Preferably, when n = 0 then m represents 1 to 5 so that the metal M of the compounds of formula I has an 18 electron count. In other words, when metal M of the compounds of formula I is iron, the total number of electrons contributed by the ligands $L_2$ is typically five.

In a particularly preferred alternative embodiment of the present invention, in a compound of formula I, n = 0, $L_2$ is as defined herein and m = 3 or 4, particularly 3.

Preferably, when n is equal to zero and m is not equal to zero in a compound of formula I, $L_2$ represents one or more ligands each of which are independently selected from lower alkyl, halo, -CO, $-P(R^{43})(R^{44})R^{45}$ or $-N(R^{46})(R^{47})R^{48}$. More preferably, $L_2$ represents one or more ligands each of which are independently selected from unsubstituted $C_1$ to $C_4$ alkyl, halo, particularly chloro, -CO, $-P(R^{43})(R^{44})R^{45}$ or $-N(R^{46})(R^{47})R^{48}$, wherein $R^{43}$ to $R^{48}$ are independently selected from hydrogen, unsubstituted $C_1$ to $C_6$ alkyl or aryl, such as phenyl.

Suitably, the metal M or metal cation thereof in the compounds of formula I is typically bonded to the cyclopentadienyl ring(s), the cyclopentadienyl moiety of the indenyl ring(s) if present, the aryl ring if present, and/or the ligands $L_2$ if present. Typically, the cyclopentadienyl ring or the cyclopentadienyl moiety of the indenyl ring exhibits a pentahapto bonding mode with the metal; however other bonding modes between the cyclopentadienyl ring or cyclopentadienyl moiety of the indenyl ring and the metal, such as trihapto coordination, are also embraced by the scope of the present invention.

Preferably, in the compound of formula I, M represents Cr, Mo, Fe, Co or Ru, or a metal cation thereof. Even more preferably, M represents Cr, Fe, Co or Ru or a metal cation thereof. Most preferably, M is selected from a Group VIIIB metal or metal cation thereof. An especially

preferred Group VIIIB metal is Fe. Although the metal M as defined herein may be in a cationic form, preferably it carries essentially no residual charge due to coordination with $L_1$ and/or $L_2$ as defined herein.

In the compound of formula I, preferably each $Q^1$ and $Q^2$, and $Q^3$, $Q^4$ and $Q^5$ (when present) are the same. Most preferably, each $Q^1$ and $Q^2$, and $Q^3$, $Q^4$ and $Q^5$ (when present), represents phosphorus.

Preferably, in the compound of formula I, $A_1$ and $A_2$, and $A_3$, $A_4$ and $A_5$ (when present), each independently represent $C_1$ to $C_6$ alkylene which is optionally substituted as defined herein, for example with lower alkyl groups. Suitably, $A_1$ and $A_2$, and $A_3$, $A_4$ and $A_5$ (when present) may include a chiral carbon atom. Preferably, the lower alkylene groups which $A_1$ to $A_5$ may represent are non-substituted. A particular preferred lower alkylene, which $A_1$ to $A_5$ may independently represent, is $-CH_2-$ or $-C_2H_4-$. Most preferably, each of $A_1$ and $A_2$, and $A_3$, $A_4$ and $A_5$ (when present), represent the same lower alkylene as defined herein, particularly $-CH_2-$.

Preferably, in the compound of formula I, $X^1$ and $X^2$ represent identical substituents, $X^3$ and $X^4$ represent identical substituents, $X^5$ and $X^6$ (when present) represent identical substituents, $X^7$ and $X^8$ (when present) represent identical substituents, and $X^9$ and $X^{10}$ (when present) represent identical substituents. More preferably, $X^1$, $X^2$, $X^3$, $X^4$ and $X^5$ to $X^{10}$ (when present) are identical.

Preferably in the compound of formula I, $R^1$ to $R^{18}$ (when present) and $R^{31}$ to $R^{42}$ (when present) each independently

represent lower alkyl, trifluoromethyl or aryl. More preferably, $R^1$ to $R^{18}$ and $R^{31}$ to $R^{42}$ each independently represent $C_1$ to $C_6$ alkyl, $C_1$-$C_6$ alkyl phenyl (wherein the phenyl group is optionally substituted as defined herein) or phenyl (wherein the phenyl group is optionally substituted as defined herein). Even more preferably, $R^1$ to $R^{18}$ and $R^{31}$ to $R^{42}$ each independently represent $C_1$ to $C_6$ alkyl, which is optionally substituted as defined herein, or trifluoromethyl. Most preferably, $R^1$ to $R^{18}$ and $R^{31}$ to $R^{42}$ each independently represent non-substituted $C_1$ to $C_6$ alkyl such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, pentyl, hexyl and cyclohexyl or trifluoromethyl.

Alternatively, or additionally, the groups $R^1$ to $R^3$, $R^4$ to $R^6$, $R^7$ to $R^9$, $R^{10}$ to $R^{12}$, $R^{13}$ to $R^{15}$, $R^{16}$ to $R^{18}$, $R^{31}$ to $R^{33}$, $R^{34}$ to $R^{36}$, $R^{37}$ to $R^{39}$ or $R^{40}$ to $R^{42}$ (when present) together independently may form cyclic alkyl structures such as 1-norbornyl or 1-norbornadienyl.

Alternatively, or additionally, the groups $R^1$ and $R^2$, $R^4$ and $R^5$, $R^7$ and $R^8$, $R^{10}$ and $R^{11}$, $R^{13}$ and $R^{14}$, $R^{16}$ and $R^{17}$, $R^{31}$ and $R^{32}$, $R^{34}$ and $R^{35}$, $R^{37}$ and $R^{38}$ or $R^{40}$ and $R^{41}$ (when present) together independently may form cyclic alkyl structures, such as cyclohexyl, and $R^3$, $R^6$, $R^9$, $R^{12}$, $R^{15}$, $R^{18}$, $R^{33}$, $R^{36}$, $R^{39}$ and $R^{42}$ (when present) each independently represent lower alkyl, trifluoromethyl or aryl as defined above.

Preferably, $R^1$, $R^4$, $R^7$, $R^{10}$, $R^{13}$, $R^{16}$, $R^{31}$, $R^{34}$, $R^{37}$ and $R^{40}$ (when present), each represent the same substituent as defined herein; $R^2$, $R^5$, $R^8$, $R^{11}$, $R^{14}$, $R^{17}$, $R^{32}$, $R^{35}$, $R^{38}$ and $R^{41}$ (when present), each represent the same substituent as

defined herein; and $R^3$, $R^6$, $R^9$, $R^{12}$, $R^{15}$, $R^{18}$, $R^{33}$, $R^{36}$, $R^{39}$ and $R^{42}$ (when present), each represent the same substituent as defined herein. More preferably $R^1$, $R^4$, $R^7$, $R^{10}$, $R^{13}$, $R^{16}$, $R^{31}$, $R^{34}$, $R^{37}$ and $R^{40}$ (when present) each represent the same $C_1$-$C_6$ alkyl, particularly non-substituted $C_1$-$C_6$ alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, pentyl, hexyl or cyclohexyl, or trifluoromethyl; $R^2$, $R^5$, $R^8$, $R^{11}$, $R^{14}$, $R^{17}$, $R^{32}$, $R^{35}$, $R^{38}$ and $R^{41}$ (when present), each independently represent the same $C_1$-$C_6$ alkyl as defined above, or trifluoromethyl; and $R^3$, $R^6$, $R^9$, $R^{12}$, $R^{15}$, $R^{18}$, $R^{33}$, $R^{36}$, $R^{39}$ and $R^{42}$ (when present), each independently represent the same $C_1$-$C_6$ alkyl as defined above, or trifluoromethyl. For example: $R^1$, $R^4$, $R^7$, $R^{10}$, $R^{13}$ and $R^{16}$ (when present) each represent methyl; $R^2$, $R^5$, $R^8$, $R^{11}$, $R^{14}$ and $R^{17}$ each represent ethyl (when present); and, $R^3$, $R^6$, $R^9$, $R^{12}$, $R^{15}$ and $R^{18}$ (when present) each represent n-butyl or n-pentyl.

In an especially preferred embodiment of the present invention each $R^1$ to $R^{18}$ and $R^{31}$ to $R^{42}$ group (when present) represents the same substituent as defined herein. Preferably, each $R^1$ to $R^{18}$ and $R^{31}$ to $R^{42}$ group represents the same $C_1$ to $C_6$ alkyl group, particularly non-substituted $C_1$-$C_6$ alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, pentyl, hexyl and cyclohexyl, or trifluoromethyl. Most preferably, each $R^1$ to $R^{18}$ and $R^{31}$ to $R^{42}$ group represents non-substituted $C_1$-$C_6$ alkyl, particularly methyl.

In a particularly preferred embodiment of the present invention, in the compound of formula I, $X^1$ represents $CR^1(R^2)(R^3)$, $X^2$ represents $CR^4(R^5)(R^6)$, $X^3$ represents

$CR^7(R^8)(R^9)$ and $X^4$ represents $CR^{10}(R^{11})(R^{12})$, wherein $R^1$ to $R^{12}$ are as defined herein.

In an alternative preferred embodiment of the present invention, in the compound of formula I, $X^1$ represents an adamantyl group as defined herein and $X^2$ represents an adamantyl group as defined herein. More preferably, both $X^1$ and $X^2$ represent the same adamantyl group as defined herein. Even more preferably, $X^1$, $X^2$, $X^3$ and $X^4$ each independently represent an adamantyl group as defined herein. Most preferably, each of $X^1$ to $X^4$ represent the same adamantyl group as defined herein.

In a further alternative preferred embodiment of the present invention, in the compound of formula I, $X^1$ and $X^2$ together with $Q^2$ to which they are attached form a 2-phospha-adamantyl group as defined herein. Most preferably, $X^1$ and $X^2$ together with $Q^2$ to which they are attached form a 2-phospha-adamantyl group as defined herein and $X^3$ and $X^4$ together with $Q^1$ to which they are attached form a 2-phospha-adamantyl group as defined herein. Most preferably, $X^1$ and $X^2$ together with $Q^2$ to which they are attached and $X^3$ and $X^4$ together with $Q^1$ to which they are attached both form the same 2-phospha-adamantyl group as defined herein.

In accordance with a further alternative preferred embodiment of the present invention, preferred compounds of formula (I) include those wherein $X^1$ and $X^2$ together with $Q^2$ to which they are attached form a ring system of formula Ia as defined herein and $X^3$ and $X^4$ together with $Q^1$ to which they are attached form a ring system of formula Ib as defined herein. Preferably, $Y^1$ and $Y^2$ are identical,

especially $Y^1$ and $Y^2$ each represent oxygen. Even more preferably, $R^{50}$ to $R^{53}$ are independently selected from methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, s-butyl, t-butyl, phenyl, p-tolyl or $CF_3$. Even more preferably, $R^{49}$ and $R^{54}$ are independently selected from hydrogen, methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, s-butyl, t-butyl, phenyl, p-tolyl or $CF_3$. Even more preferably, $R^{50}$ to $R^{53}$ each represent the same group as defined herein, particularly methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, s-butyl, t-butyl, especially methyl. Even more preferably, both $R^{49}$ and $R^{54}$ represent the same group as defined herein, especially hydrogen. Most preferably, the ring system of formula Ia is identical to the ring system of formula Ib.

Preferably, in the compound of formula I, when D and E together with the carbon atoms of the cyclopentadienyl ring to which they are attached do not form an optionally substituted phenyl ring, each of K, D and E represent an identical substituent.

Preferably, in the compound of formula I, K represents $-A_3-Q^3(X^5)X^6$, hydrogen, lower alkyl, $-CF_3$, phenyl or lower alkyl phenyl. If K represents $-A_3-Q^3(X^5)X^6$, then preferably $X^5$ and $X^6$ represent identical groups as defined herein, more preferably each of $X^1$, $X^2$, $X^3$, $X^4$, $X^5$ and $X^6$ represents an identical substituent. More preferably, K represents $-A_3-Q^3(X^5)X^6$, hydrogen, phenyl, $C_1$-$C_6$ alkylphenyl, unsubstituted $C_1$-$C_6$ alkyl, such as methyl, ethyl, propyl, butyl, pentyl and hexyl, or $-CF_3$. Even more preferably, K represents hydrogen or $-A_3-Q^3(X^5)X^6$, wherein $-A_3-Q^3(X^5)X^6$ is identical to $-A_1-Q^2(X^1)X^2$ and $-A_2-Q^1(X^3)X^4$. Most preferably, K represents hydrogen in the compound of formula I.

Preferably, in the compound of formula I, D represents $-A_4-Q^4(X^7)X^8$, hydrogen, lower alkyl, $CF_3$, phenyl or lower alkylphenyl, and E represents $-A_5-Q^5(X^9)X^{10}$, hydrogen, lower alkyl, $CF_3$, phenyl or lower alkylphenyl, or D and E together with the carbons of the cyclopentadienyl ring to which they are attached form an optionally substituted phenyl ring.

If D represents $-A_4-Q^4(X^7)X^8$, then preferably both $X^7$ and $X^8$ represent identical substituents as defined herein, more preferably each of $X^1$, $X^2$, $X^3$, $X^4$, $X^7$ and $X^8$ represents an identical substituent.

If E represents $-A_5-Q^5(X^9)X^{10}$, then preferably both $X^9$ and $X^{10}$ represent identical substituents as defined herein, more preferably each of $X^1$, $X^2$, $X^3$, $X^4$, $X^9$ and $X^{10}$ represents an identical substituent.

If K represents $-A_3-Q^3(X^5)X^6$ and E represents $-A_5-Q^5(X^9)X^{10}$, then preferably $X^1$ to $X^{10}$ are identical.

Preferably, in the compound of formula I, D represents $-A_4-Q^4(X^7)X^8$, hydrogen, phenyl, $C_1$-$C_6$ alkylphenyl, unsubstituted $C_1$-$C_6$ alkyl, such as methyl, ethyl, propyl, butyl, pentyl and hexyl, or $CF_3$; E represents $-A_5-Q^5(X^9)X^{10}$, hydrogen, phenyl, $C_1$-$C_6$ alkylphenyl, unsubstituted $C_1$-$C_6$ alkyl such as methyl, ethyl, propyl, butyl, pentyl and hexyl, or $-CF_3$; or both D and E together with the carbon atoms of the cyclopentadienyl ring to which they are attached form a phenyl ring which is optionally substituted with one or more group selected from phenyl, $C_1$-$C_6$ alkylphenyl, unsubstituted $C_1$-$C_6$ alkyl or $-CF_3$. More

preferably, in the compound of formula I, D represents hydrogen or $-A_4-Q^4(X^7)X^8$, wherein $-A_4-Q^4(X^7)X^8$ is identical to $-A_1-Q^2(X^1)X^2$ and $-A_2-Q^1(X^3)X^4$; E represents hydrogen or $-A_5-Q^5(X^9)X^{10}$, wherein $-A_5-Q^5(X^9)X^{10}$ is identical to $-A_1-Q^2(X^1)X^2$ and $-A_2-Q^1(X^3)X^4$; or both D and E together with the carbon atoms of the cyclopentadienyl ring to which they are attached form an unsubstituted phenyl ring i.e. it bears only hydrogen atoms. Most preferably, both D and E represent hydrogen or D and E together with the carbon atoms of the cyclopentadienyl ring to which they are attached form an unsubstituted phenyl ring. An especially preferred compound of formula I is where both D and E represent hydrogen.

Especially preferred compounds of formula I include those wherein:

(1) $X^1$ represents $CR^1(R^2)(R^3)$, $X^2$ represents $CR^4(R^5)(R^6)$, $X^3$ represents $CR^7(R^8)(R^9)$, $X^4$ represents $CR^{10}(R^{11})(R^{12})$, wherein each of $R^1$ to $R^{12}$ independently represents unsubstituted $C_1$-$C_6$ alkyl or trifluoromethyl, particularly where each of $R^1$ to $R^{12}$ is identical, especially where each of $R^1$ to $R^{12}$ represents methyl;
$A_1$ and $A_2$ are the same and represent $-CH_2-$;
K, D and E are the same and represent hydrogen or unsubstituted $C_1$-$C_6$ alkyl, particularly hydrogen;
$Q^1$ and $Q^2$ both represent phosphorus;
M represents Fe;
n = 1 and $L_1$ represents cyclopentadienyl, and m = 0.

(2) $X^1$ represents $CR^1(R^2)(R^3)$, $X^2$ represents $CR^4(R^5)(R^6)$, $X^3$ represents $CR^7(R^8)(R^9)$, $X^4$ represents $CR^{10}(R^{11})(R^{12})$;

K represents $-CH_2-Q^3(X^5)X^6$ wherein $X^5$ represents $CR^{13}(R^{14})(R^{15})$ and $X^6$ represents $CR^{16}(R^{17})(R^{18})$; each of $R^1$ to $R^{18}$ independently represent unsubstituted $C_1$-$C_6$ alkyl or trifluoromethyl, particularly where each of $R^1$ to $R^{18}$ is identical, especially where each of $R^1$ to $R^{18}$ represents methyl;
$A_1$ and $A_2$ are the same and represent $-CH_2-$;
$Q^1$, $Q^2$ and $Q^3$ each represent phosphorus;
D and E are the same and represent hydrogen or unsubstituted $C_1$-$C_6$ alkyl, particularly hydrogen;
M represents Fe;
n = 1 and $L_1$ represents cyclopentadienyl, and m = 0.

(3) $X^1$ represents $CR^1(R^2)(R^3)$, $X^2$ represents $CR^4(R^5)(R^6)$, $X^3$ represents $CR^7(R^8)(R^9)$, $X^4$ represents $CR^{10}(R^{11})(R^{12})$;
K represents $-CH_2-Q^3(X^5)X^6$ wherein $X^5$ represents $CR^{13}(R^{14})(R^{15})$ and $X^6$ represents $CR^{16}(R^{17})(R^{18})$;
each of $R^1$ to $R^{18}$ independently represent unsubstituted $C_1$-$C_6$ alkyl or trifluoromethyl, particularly where each of $R^1$ to $R^{18}$ is identical, especially where each of $R^1$ to $R^{18}$ represents methyl;
$A_1$ and $A_2$ are the same and represent $-CH_2-$;
$Q^1$, $Q^2$ and $Q^3$ each represent phosphorus;
D and E together with the carbon atoms of the cyclopentadienyl ring to which they are attached form an unsubstituted phenyl ring;
M represents Fe;
n = 1 and $L_1$ represents cyclopentadienyl, and m = 0.

(4) $X^1$ represents $CR^1(R^2)(R^3)$, $X^2$ represents $CR^4(R^5)(R^6)$, $X^3$ represents $CR^7(R^8)(R^9)$, $X^4$ represents $CR^{10}(R^{11})(R^{12})$, wherein each of $R^1$ to $R^{12}$ independently represent unsubstituted $C_1$-$C_6$ alkyl or trifluoromethyl,

particularly where each of $R^1$ to $R^{12}$ is identical, especially where each of $R^1$ to $R^{12}$ represents methyl;
$A_1$ and $A_2$ are the same and represent $-CH_2-$;
$Q^1$ and $Q^2$ both represent phosphorus;
K represents hydrogen or $C_1$-$C_6$ alkyl, particularly hydrogen;
D and E together with the carbon atoms of the cyclopentadienyl ring to which they are attached form an unsubstituted phenyl ring;
M represents Fe;
n = 1 and $L_1$ represents cyclopentadienyl, and m = 0.

(5) $X^1$ represents $CR^1(R^2)(R^3)$, $X^2$ represents $CR^4(R^5)(R^6)$, $X^3$ represents $CR^7(R^8)(R^9)$, $X^4$ represents $CR^{10}(R^{11})(R^{12})$;
E represents $-CH_2-Q^5(X^9)X^{10}$ wherein $X^9$ represents $CR^{37}(R^{38})(R^{39})$ and $X^{10}$ represents $CR^{40}(R^{41})(R^{42})$;
each of $R^1$ to $R^{12}$ and $R^{37}$ to $R^{42}$ independently represent unsubstituted $C_1$-$C_6$ alkyl or trifluoromethyl, particularly where each of $R^1$ to $R^{12}$ and $R^{37}$ to $R^{42}$ is identical, especially where each of $R^1$ to $R^{12}$ and $R^{37}$ to $R^{42}$ represents methyl;
$A_1$ and $A_2$ are the same and represent $-CH_2-$;
$Q^1$, $Q^2$ and $Q^5$ each represent phosphorus;
D and K are the same and represent hydrogen or unsubstituted $C_1$-$C_6$ alkyl, particularly hydrogen;
M represents Fe;
n = 1 and $L_1$ represents cyclopentadienyl, and m = 0.

(6) $X^1$ represents $CR^1(R^2)(R^3)$, $X^2$ represents $CR^4(R^5)(R^6)$, $X^3$ represents $CR^7(R^8)(R^9)$, $X^4$ represents $CR^{10}(R^{11})(R^{12})$;
K represents $-CH_2-Q^3(X^5)X^6$ wherein $X^5$ represents $CR^{13}(R^{14})(R^{15})$ and $X^6$ represents $CR^{16}(R^{17})(R^{18})$;

D represents $-CH_2-Q^4(X^7)X^8$ wherein $X^7$ represents $CR^{31}(R^{32})(R^{33})$ and $X^8$ represents $CR^{34}(R^{35})(R^{36})$;
E represents $-CH_2-Q^5(X^9)X^{10}$ wherein $X^9$ represents $CR^{37}(R^{38})(R^{39})$ and $X^{10}$ represents $CR^{40}(R^{41})(R^{42})$;
each of $R^1$ to $R^{18}$ and $R^{31}$ to $R^{42}$ independently represent unsubstituted $C_1$-$C_6$ alkyl or trifluoromethyl, particularly where each of $R^1$ to $R^{18}$ and $R^{31}$ to $R^{42}$ is identical, especially where each of $R^1$ to $R^{18}$ and $R^{31}$ to $R^{42}$ represents methyl;
$A_1$ and $A_2$ are the same and represent $-CH_2-$;
$Q^1$, $Q^2$, $Q^3$, $Q^4$ and $Q^5$ each represent phosphorus
M represents Fe;
n = 1 and $L_1$ represents cyclopentadienyl; and m = 0.

(7) $X^1$, $X^2$, $X^3$ and $X^4$ independently represent adamantyl, especially where $X^1$ to $X^4$ represent the same adamantyl group;
$A_1$ and $A_2$ are the same and represent $-CH_2-$;
K, D and E are the same and represent hydrogen or unsubstituted $C_1$-$C_6$ alkyl, particularly hydrogen;
$Q^1$ and $Q^2$ both represent phosphorus;
M represents Fe;
n = 1 and $L_1$ represents cyclopentadienyl, and m = 0.

(8) $X^1$, $X^2$, $X^3$ and $X^4$ independently represent adamantyl, especially where $X^1$ to $X^4$ represent the same adamantyl group;
K represents $-CH_2-Q^3(X^5)X^6$ wherein $X^5$ and $X^6$ independently represent adamantyl, especially where $X^1$ to $X^6$ represent the same adamantyl group;
$A_1$ and $A_2$ are the same and represent $-CH_2-$;
$Q^1$, $Q^2$ and $Q^3$ each represent phosphorus;

D and E are the same and represent hydrogen or unsubstituted $C_1$-$C_6$ alkyl, particularly hydrogen;
M represents Fe;
n = 1 and $L_1$ represents cyclopentadienyl, and m = 0.

(9) $X^1$, $X^2$, $X^3$ and $X^4$ independently represent adamantyl, especially where $X^1$ to $X^4$ represent the same adamantyl group;
K represents $-CH_2-Q^3(X^5)X^6$ wherein $X^5$ and $X^6$ independently represent adamantyl, especially where $X^1$ to $X^6$ represent the same adamantyl group;
$A_1$ and $A_2$ are the same and represent $-CH_2-$;
$Q^1$, $Q^2$ and $Q^3$ each represent phosphorus;
D and E together with the carbon atoms of the cyclopentadienyl ring to which they are attached form an unsubstituted phenyl ring;
M represents Fe;
n = 1 and $L_1$ represents cyclopentadienyl, and m = 0.

(10) $X^1$, $X^2$, $X^3$ and $X^4$ independently represent adamantyl, especially where $X^1$ to $X^4$ represent the same adamantyl group;
$A_1$ and $A_2$ are the same and represent $-CH_2-$;
$Q^1$ and $Q^2$ both represent phosphorus;
K represents hydrogen or unsubstituted $C_1$-$C_6$ alkyl, particularly hydrogen;
D and E together with the carbon atoms of the cyclopentadienyl ring to which they are attached form an unsubstituted phenyl ring;
M represents Fe;
n = 1 and $L_1$ represents cyclopentadienyl, and m = 0.

(11) $X^1$, $X^2$, $X^3$ and $X^4$ independently represent adamantyl;

K represents $-CH_2-Q^3(X^5)X^6$ wherein $X^5$ and $X^6$ independently represent adamantyl;
D represents $-CH_2-Q^4(X^7)X^8$ wherein $X^7$ and $X^8$ independently represents adamantyl;
E represents $-CH_2-Q^5(X^9)X^{10}$ wherein $X^9$ and $X^{10}$ independently represents adamantyl, especially where $X^1$ to $X^{10}$ represent the same adamantyl group;
$A_1$ and $A_2$ are the same and represent $-CH_2-$;
$Q^1$, $Q^2$, $Q^3$, $Q^4$ and $Q^5$ each represent phosphorus;
M represents Fe;
n = 1 and $L_1$ represents cyclopentadienyl; and m = 0.

(12) $X^1$ and $X^2$ together with $Q^2$ to which they are attached represents 2-phospha-adamantyl;
$X^3$ and $X^4$ together with $Q^1$ to which they are attached represents 2-phospha-adamantyl;
$A_1$ and $A_2$ are the same and represent $-CH_2-$;
K, D and E are the same and represent hydrogen or unsubstituted $C_1$-$C_6$ alkyl, particularly hydrogen;
$Q^1$ and $Q^2$ both represent phosphorus;
M represents Fe;
n = 1 and $L_1$ represents cyclopentadienyl, and m = 0.

(13) $X^1$ and $X^2$ together with $Q^2$ to which they are attached represents 2-phospha-adamantyl;
$X^3$ and $X^4$ together with $Q^1$ to which they are attached represents 2-phospha-adamantyl;
K represents $-CH_2-Q^3(X^5)X^6$ wherein $X^5$ and $X^6$ together with $Q^3$ to which they are attached represents 2-phospha-adamantyl;
$A_1$ and $A_2$ are the same and represent $-CH_2-$;
$Q^1$, $Q^2$ and $Q^3$ each represent phosphorus;

D and E are the same and represent hydrogen or unsubstituted $C_1$-$C_6$ alkyl, particularly hydrogen;

M represents Fe;

n = 1 and $L_1$ represents cyclopentadienyl, and m = 0.

(14) $X^1$ and $X^2$ together with $Q^2$ to which they are attached represents 2-phospha-adamantyl;

$X^3$ and $X^4$ together with $Q^1$ to which they are attached represents 2-phospha-adamantyl;

K represents $-CH_2-Q^3(X^5)X^6$ wherein $X^5$ and $X^6$ together with $Q^3$ to which they are attached represents 2-phospha-adamantyl;

$A_1$ and $A_2$ are the same and represent $-CH_2-$;

$Q^1$, $Q^2$ and $Q^3$ each represent phosphorus;

D and E together with the carbon atoms of the cyclopentadienyl ring to which they are attached form an unsubstituted phenyl ring;

M represents Fe;

n = 1 and $L_1$ represents cyclopentadienyl, and m = 0.

(15) $X^1$ and $X^2$ together with $Q^2$ to which they are attached represents 2-phospha-adamantyl;

$X^3$ and $X^4$ together with $Q^1$ to which they are attached represents 2-phospha-adamantyl;

$A_1$ and $A_2$ are the same and represent $-CH_2-$;

$Q^1$ and $Q^2$ both represent phosphorus;

K represents hydrogen or unsubstituted $C_1$-$C_6$ alkyl, particularly hydrogen;

D and E together with the carbon atoms of the cyclopentadienyl ring to which they are attached form an unsubstituted phenyl ring;

M represents Fe;

n = 1 and $L_1$ represents cyclopentadienyl, and m = 0.

(16) $X^1$ and $X^2$ together with $Q^2$ to which they are attached represents 2-phospha-adamantyl;
$X^3$ and $X^4$ together with $Q^1$ to which they are attached represents 2-phospha-adamantyl;
K represents $-CH_2-Q^3(X^5)X^6$ wherein $X^5$ and $X^6$ together with $Q^3$ to which they are attached represents 2-phospha-adamantyl;
D represents $-CH_2-Q^4(X^7)X^8$ wherein $X^7$ and $X^8$ together with $Q^4$ to which they are attached represents 2-phospha-adamantyl;
E represents $-CH_2-Q^5(X^9)X^{10}$ wherein $X^9$ and $X^{10}$ together with $Q^5$ to which they are attached represents 2-phospha-adamantyl;
$A_1$ and $A_2$ are the same and represent $-CH_2-$;
$Q^1$, $Q^2$, $Q^3$, $Q^4$ and $Q^5$ each represent phosphorus
M represents Fe;
n = 1 and $L_1$ represents cyclopentadienyl; and m = 0.

(17) $X^1$ and $X^2$ together with $Q^2$ to which they are attached form a ring system of formula Ia, $X^3$ and $X^4$ together with $Q^1$ to which they are attached form a ring system of formula Ib, wherein $Y^1$ and $Y^2$ both represent oxygen, $R^{50}$ to $R^{53}$ are independently selected from unsubstituted $C_1$-$C_6$ alkyl or $CF_3$, and $R^{49}$ and $R^{54}$ represent hydrogen;
$A_1$ and $A_2$ are the same and represent $-CH_2-$;
K, D and E are the same and represent hydrogen or unsubstituted $C_1$-$C_6$ alkyl, particularly hydrogen;
$Q^1$ and $Q^2$ both represent phosphorus;
M represents Fe;
n = 1 and $L_1$ represents cyclopentadienyl, and m = 0.

(18) $X^1$ and $X^2$ together with $Q^2$ to which they are attached form a ring system of formula Ia, $X^3$ and $X^4$ together with $Q^1$ to which they are attached form a ring system of formula Ib, wherein $Y^1$ and $Y^2$ both represent oxygen, $R^{50}$ to $R^{53}$ are independently selected from unsubstituted $C_1$-$C_6$ alkyl or $CF_3$, and $R^{49}$ and $R^{54}$ represent hydrogen;

K represents $-CH_2-Q^3(X^5)X^6$ wherein $X^5$ and $X^6$ together with $Q^3$ to which they are attached form a ring system of formula Ic, wherein $Y^3$ represents oxygen, $R^{50}$ to $R^{53}$ are independently selected from hydrogen, unsubstituted $C_1$-$C_6$ alkyl or $CF_3$ and $R^{49}$ and $R^{54}$ represent hydrogen;

$A_1$ and $A_2$ are the same and represent $-CH_2-$;

$Q^1$, $Q^2$ and $Q^3$ each represent phosphorus;

D and E are the same and represent hydrogen or $C_1$-$C_6$ alkyl, particularly hydrogen;

M represents Fe;

n = 1 and $L_1$ represents cyclopentadienyl, and m = 0.

(19) $X^1$ and $X^2$ together with $Q^2$ to which they are attached form a ring system of formula Ia, $X^3$ and $X^4$ together with $Q^1$ to which they are attached form a ring system of formula Ib, wherein $Y^1$ and $Y^2$ both represent oxygen, $R^{50}$ to $R^{53}$ are independently selected from unsubstituted $C_1$-$C_6$ alkyl or $CF_3$, and $R^{49}$ and $R^{54}$ represent hydrogen;

K represents $-CH_2-Q^3(X^5)X^6$ wherein $X^5$ and $X^6$ together with $Q^3$ to which they are attached form a ring system of formula Ic, wherein $Y^3$ represents oxygen, $R^{50}$ to $R^{53}$ are independently selected from unsubstituted $C_1$-$C_6$ alkyl or $CF_3$, and $R^{49}$ and $R^{54}$ represent hydrogen;

$A_1$ and $A_2$ are the same and represent $-CH_2-$;
$Q^1$, $Q^2$ and $Q^3$ each represent phosphorus;
D and E together with the carbon atoms of the cyclopentadienyl ring to which they are attached form an unsubstituted phenyl ring;
M represents Fe;
n = 1 and $L_1$ represents cyclopentadienyl, and m = 0.

(20) $X^1$ and $X^2$ together with $Q^2$ to which they are attached form a ring system of formula Ia, $X^3$ and $X^4$ together with $Q^1$ to which they are attached form a ring system of formula Ib, wherein $Y^1$ and $Y^2$ both represent oxygen, $R^{50}$ to $R^{53}$ are independently selected from unsubstituted $C_1$-$C_6$ alkyl or $CF_3$, and $R^{49}$ and $R^{54}$ represent hydrogen;
$A_1$ and $A_2$ are the same and represent $-CH_2-$;
$Q^1$ and $Q^2$ both represent phosphorus;
K represents hydrogen or unsubstituted $C_1$-$C_6$ alkyl, particularly hydrogen;
D and E together with the carbon atoms of the cyclopentadienyl ring to which they are attached form an unsubstituted phenyl ring;
M represents Fe;
n = 1 and $L_1$ represents cyclopentadienyl, and m = 0.

(21) $X^1$ and $X^2$ together with $Q^2$ to which they are attached form a ring system of formula Ia, $X^3$ and $X^4$ together with $Q^1$ to which they are attached form a ring system of formula Ib, wherein $Y^1$ and $Y^2$ both represent oxygen, $R^{50}$ to $R^{53}$ are independently selected from unsubstituted $C_1$-$C_6$ alkyl or $CF_3$, and $R^{49}$ and $R^{54}$ represent hydrogen;

K represents $-CH_2-Q^3(X^5)X^6$ wherein $X^5$ and $X^6$ together with $Q^3$ to which they are attached form a ring system of formula Ic, wherein $Y^3$ represents oxygen, $R^{50}$ to $R^{53}$ are independently selected from unsubstituted $C_1$-$C_6$ alkyl or $CF_3$, and $R^{49}$ and $R^{54}$ represent hydrogen;

D represents $-CH_2-Q^4(X^7)X^8$ wherein $X^7$ and $X^8$ together with $Q^4$ to which they are attached form a ring system of formula Ic, wherein $Y^3$ represents oxygen, $R^{50}$ to $R^{53}$ are independently selected from unsubstituted $C_1$-$C_6$ alkyl or $CF_3$, and $R^{49}$ and $R^{54}$ represent hydrogen;

E represents $-CH_2-Q^5(X^9)X^{10}$ wherein $X^9$ and $X^{10}$ together with $Q^5$ to which they are attached form a ring system of formula Ie, wherein $Y^5$ represents oxygen, and $R^{50}$ to $R^{53}$ are independently selected from unsubstituted $C_1$-$C_6$ alkyl or $CF_3$, and $R^{49}$ and $R^{54}$ represent hydrogen;

$A_1$ and $A_2$ are the same and represent $-CH_2-$;

$Q^1$, $Q^2$, $Q^3$, $Q^4$ and $Q^5$ each represent phosphorus;

M represents Fe;

n = 1 and $L_1$ represents cyclopentadienyl; and m = 0.

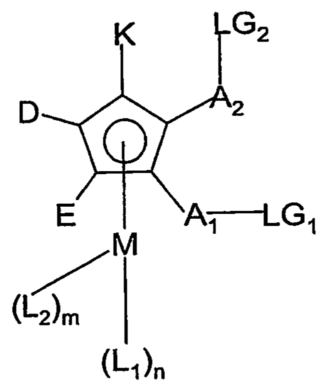
According to a second aspect, the present invention provides a process for preparing the compounds of the invention comprising combining (a) a Group VIIIB metal or compound thereof, as defined herein; with (b) a compound of formula I as defined herein. Conveniently, the compounds of the invention may be obtained by dissolving the Group VIIIB metal or compound thereof as defined herein in a suitable solvent such as the ultimate end product of the carbonylation reaction, for example methylpropanoate where the ethylenically unsaturated

compound to be carbonylated is ethene in the presence of methanol or methylnonanoate where it is intended to carbonylate octene in the presence of methanol. Preferably, the reactants are mixed at room temperature under an inert atmosphere (e.g. under nitrogen). The molar ratio of the compound of formula I (referred to as (b)) to the Group VIIIB metal or compound thereof (referred to as (a)) is preferably in the range of 1:1 to 5:1, more preferably in the range of 1:1 to 3:1, most preferably in the range of 1:1 to 1:1.25. Conveniently, the possibility of applying these low molar ratios is advantageous, as it avoids the use of an excess of the compound of formula I and hence minimises the consumption of these usually expensive compounds. Suitably, the compounds of the invention are prepared in a separate step preceding their use in-situ in the carbonylation reaction of an ethylenically unsaturated compound. As mentioned previously, the compounds of the invention may include additional anions derivable from the Group VIIIB compound thereof, if one is employed, and/or by the addition of a separate source of anions. If a separate source of anions is employed these may be added to the compounds of the invention prior to use in the carbonylation reaction. Alternatively, or additionally, a separate source of anions may be added to the carbonylation reaction.

According to a third aspect, the present invention provides a compound of formula I as defined herein.

According to a fourth aspect, the present invention provides a process for the preparation of a compound of formula I, which comprises the reaction of a compound of formula II wherein $A_1$, $A_2$, K, D, E, M, $L_1$, $L_2$, n and m are

as defined for a compound of formula I, and $LG_1$ and $LG_2$ represent suitable leaving groups,




(II)

with a compound of formula IIIa and IIIb

$HQ^2(X^1)X^2$

(IIIa)

$HQ^1(X^3)X^4$

(IIIb)

wherein $X^1$ represents $CR^1(R^2)(R^3)$ or adamantyl, $X^2$ represents $CR^4(R^5)(R^6)$ or adamantyl, or $X^1$ and $X^2$ together with $Q^2$ to which they are attached form a 2-phospha-adamantyl group, or $X^1$ and $X^2$ together with $Q^2$ to which they are attached form a ring system of formula Ia;

wherein $X^3$ represents $CR^7(R^8)(R^9)$ or adamantyl, $X^4$ represents $CR^{10}(R^{11})(R^{12})$ or adamantyl, or $X^3$ and $X^4$ together with $Q^1$ to which they are attached form a 2-phospha-adamantyl group, or $X^3$ and $X^4$ together with $Q^1$ to which they are attached form a ring system of formula Ib;

$R^1$ to $R^{12}$, adamantyl, $Q^1$ and $Q^2$, 2-phospha-adamantyl, and the ring systems of formula Ia and Ib are as defined for a compound of formula I.

Suitable leaving groups which $LG_1$ and $LG_2$ may independently represent include groups which are readily displaced by nucleophilic attack by the phosphine , arsine or stibene derivatives IIIa and IIIb. Examples of such groups include halo, particularly bromo and iodo, $-NR^{23}R^{24}$ where $R^{23}$ and $R^{24}$ both represent lower alkyl, particularly methyl, and hyroxyl whether in a protonated form or not. Preferably, $LG_1$ and $LG_2$ each independently represent $-NMe_2$ or hydroxyl. Most preferably, both $LG_1$ and $LG_2$ represent $-NMe_2$, or $LG_1$ and $LG_2$ represent $NMe_2$ or hydroxyl, respectively.

The reaction may be accomplished using methods which are well known to those skilled in the art. For example, the reaction may be accomplished by heating a solution of a compound of formula II with a compound of formula IIIa and IIIb in anhydrous acetic acid at a temperature between 70 to 90°C, preferably approximately 80°C under an inert atmosphere, such as a nitrogen atmosphere.

Preferably, when the compound of formula IIIa represents $HQ^2(CR^1(R^2)(R^3))CR^4(R^5)(R^6)$ then the compound of formula IIIb represents $HQ^1(CR^7(R^8)(R^9))CR^{10}(R^{11})(R^{12})$, wherein $Q^1$ is the same as $Q^2$ and $R^1$ is the same as $R^7$, $R^2$ is the same as $R^8$, $R^3$ is the same as $R^9$, $R^4$ is the same as $R^{10}$, $R^5$ is the same as $R^{11}$, and $R^6$ is the same as $R^{12}$.

Preferably, when the compound of formula IIIa represents $HQ^2(X^1)X^2$ wherein $X^1$ and $X^2$ independently represent adamantyl, then the compound of formula IIIb represents $HQ^1(X^3)X^4$ wherein $X^3$ and $X^4$ independently represent adamantyl. More preferably, $X^1$ represents the same

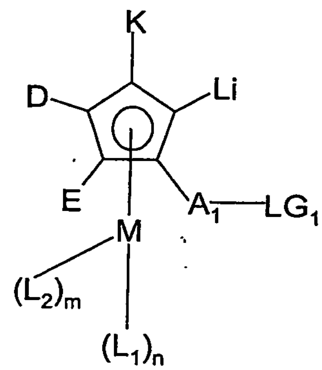
adamantyl group as $X^3$, $X^2$ represents the same adamantyl group as $X^4$, and $Q^1$ is the same as $Q^2$.

Preferably, when the compound of formula IIIa represents $HQ^2(X^1)X^2$ wherein $X^1$ and $X^2$ together with $Q^2$ to which they are attached form a 2-phospha-adamantyl group, then the compound of formula IIIb represents $HQ^1(X^3)X^4$ wherein $X^3$ and $X^4$ together with $Q^1$ to which they are attached form a 2-phospha-adamantyl group. More preferably, $X^1$ and $X^2$ together with $Q^2$ forms the same 2-phospha-adamantyl group formed by the combination of $X^3$ and $X^4$ together with $Q^1$.

Preferably, when the compound of formula IIIa represents $HQ^2(X^1)X^2$ wherein $X^1$ and $X^2$ together with $Q^2$ to which they are attached form a ring system of formula Ia, then the compound of formula IIIb represents $HQ^1(X^3)X^4$ where $X^3$ and $X^4$ together with $Q^1$ to which they are attached form a ring system of formula Ib. Preferably, the ring system of formula Ia is the same as the ring system of formula Ib.

Most preferably, the compound of formula IIIa is identical to the compound of formula IIIb.

A compound of formula II, where $LG_2$ represents hydroxyl or $NR^{23}R^{24}$, may be prepared by reaction of a compound of formula IV, wherein $A_1$, $LG_1$, K, D, E, M, $L_1$, $L_2$, n and m are as defined for a compound of formula II, and Li represents lithium,



(IV)

with a compound of formula Va

$$A_2{=}LG_2$$

(Va)

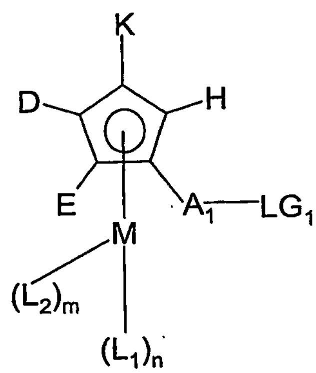
wherein $A_2$ is as defined for a compound of formula II and $LG_2$ represents oxygen (thereby forming a hydroxyl derivative following reaction with compound IV) or $NR^{23}R^{24}$. Preferably, in a compound of formula Va, $A_2$ represents methylene and $LG_2$ represents $NMe_2$. For example, a compound of formula Va may represent Eschenmosers salt $I^-CH_2N^+Me_2$ (see Glidewell C, Journal of Organometallic Chemistry, 527, (1997), p.259-261).

Alternatively, in a compound of formula Va, $A_2$ represents methylene and $LG_2$ represents oxygen. For example, a compound of formula Va may represent formaldehyde, which for practical purposes may be paraformaldehyde.

The reaction may be carried out using methods which are well known to those skilled in the art. For example, the reaction may be accomplished by stirring a solution of the compound of formula IV and Va in an appropriate solvent, such as diethyl ether, at room temperature.

Preferably, in a compound of formula IV, $LG_1$ does not represent hydroxyl, as the hydroxyl functionality will typically have to be protected prior to ortho-lithiating the precursor compound (compound VI below) to the compound of formula IV. Preferably, in a compound of formula IV, $LG_1$ represents $NR^{23}R^{24}$, most preferably $LG_1$ represents $NMe_2$.

A compound of formula IV may be prepared by ortho-lithiation of a compound of formula VI, wherein $A_1$, $LG_1$, K, D, E, M, $L_1$, $L_2$, n and m are as defined for a compound of formula IV,



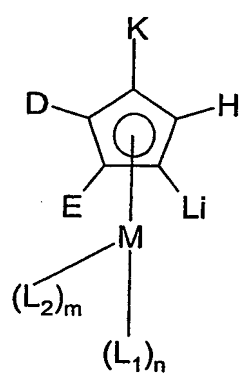
(VI)

by reaction with an alkyl lithium (e.g. n-butyl lithium). Preferably, in a compound of formula VI, $LG_1$ does not represent hydroxyl, as the hydroxyl functionality will typically have to be protected prior to performing the ortho-lithiation reaction. Preferably, in a compound of formula VI, $LG_1$ represents $NR^{23}R^{24}$, most preferably $LG_1$ represents $NMe_2$.

Typically, the ortho-lithiation reaction of compounds of formula VI with an alkyl lithium is performed in an inert

solvent, for example tetrahydrofuran or hexane, at low temperatures (e.g. -78°C), under a nitrogen atmosphere.

A compound of formula VI, where $LG_1$ represents hydroxyl or $NR^{23}R^{24}$, may be prepared from a compound of formula VII wherein K, D, E, M, $L_1$, $L_2$, n and m are as defined for a compound of formula VI and Li represents lithium




(VII)

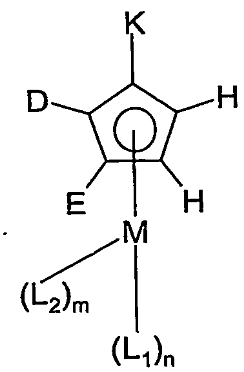
by reaction with a compound of formula Vb

$$A_1{=}LG_1$$

(Vb)

wherein $A_1$ is as defined for a compound of formula VI and $LG_1$ represents oxygen (thereby forming a hydroxyl derivative following reaction with compound VII) or $NR^{23}R^{24}$. Preferably, $LG_1$ represents $NR^{23}R^{24}$, especially $NMe_2$. In other words, a compound of formula Vb is preferably Eschenmosers salt. The reaction may be accomplished using similar conditions as described for the preparation of a compound of formula II above.

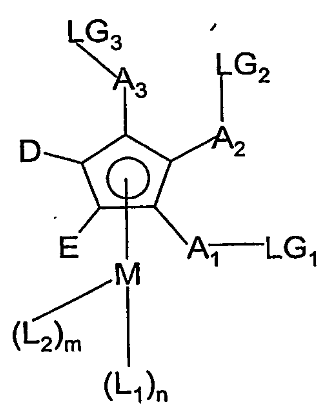
Similarly, a compound of formula VII may be prepared by lithiation of a compound of formula VIII



(VIII)

wherein K, D, E, M, $L_1$, $L_2$, n and m are as defined for a compound of formula VII.

Suitably, a compound of formula I wherein K represents $-A_3-Q^3(X^5)X^6$ may be prepared from a compound of formula IX wherein $A_1$, $A_2$, $A_3$, D, E, M, $L_1$, $L_2$, n and m are as defined for a compound of formula I, and $LG_1$, $LG_2$ and $LG_3$ represent suitable leaving groups as defined herein,



(IX)

by reaction with a compound of formula IIIa and IIIb as defined herein, and a compound of formula IIIc

$$HQ^3(X^5)X^6$$
$$\text{(IIIc)}$$

wherein $X^5$ represents $CR^{13}(R^{14})(R^{15})$ or adamantyl, $X^6$ represents $CR^{16}(R^{17})(R^{18})$ or adamantyl, or $X^5$ and $X^6$ together with $Q^3$ form a 2-phospha-adamantyl group, or $X^5$ and $X^6$ together with $Q^3$ to which they are attached form a ring system of formula Ic; and $R^{13}$ to $R^{18}$, adamantyl, $Q^3$, 2-phospha-adamantyl, and the ring system of formula Ic are as defined for a compound of formula I.

Preferably, when the compound of formula IIIa represents $HQ^2(CR^1(R^2)(R^3))CR^4(R^5)(R^6)$, then the compound of formula IIIb represents $HQ^1(CR^7(R^8)(R^9))CR^{10}(R^{11})(R^{12})$ and the compound of formula IIIc represents $HQ^3(CR^{13}(R^{14})(R^{15}))CR^{17}(R^{18})(R^{19})$, $Q^1$ is the same as $Q^2$ and $Q^3$, $R^1$ is the same as $R^7$ and $R^{13}$, $R^2$ is the same as $R^8$ and $R^{14}$, $R^3$ is the same as $R^9$ and $R^{15}$, $R^4$ is the same as $R^{10}$ and $R^{16}$, $R^5$ is the same as $R^{11}$ and $R^{17}$, and $R^6$ is the same as $R^{12}$ and $R^{18}$.

Preferably, when $X^1$ and $X^2$ in the compound of formula IIIa independently represents adamantyl, then $X^3$ and $X^4$ in the compound of formula IIIb independently represent adamantyl, and $X^5$ and $X^6$ in the compound of formula IIIc independently represent adamantyl. Most preferably, $X^1$ to $X^6$ represent the same adamantyl group.

Preferably, when $X^1$ and $X^2$ together with $Q^2$ to which they are attached in the compound of formula IIIa form a 2-phospha-adamantyl group, then $X^3$ and $X^4$ together with $Q^1$ in the compound of formula IIIb, and $X^5$ and $X^6$ together with

$Q^3$ in the compound of formula IIIc both form a 2-phospha-adamantyl group.

Preferably, when $X^1$ and $X^2$ together with $Q^2$ to which they are attached form a ring system of formula Ia, then $X^3$ and $X^4$ together with $Q^1$ to which they are attached in the compound of IIIb forms a ring system of formula Ib, and $X^5$ and $X^6$ together with $Q^3$ to which they are attached in the compound IIIc forms a ring system of formula Ic.

Most preferably, the compounds of formula IIIa, IIIb and IIIc are identical.

Suitably, $LG_3$ represents a leaving group as defined herein in respect of $LG_1$ and $LG_2$. Preferably, $LG_3$ represents $NR^{23}R^{24}$ or hydroxyl. Most preferably, $LG_3$ represents $NMe_2$, particularly when both $LG_1$ and $LG_2$ also represent $NMe_2$.

Similarly, the compound of formula IX, where $LG_3$ represents hydroxyl or $NR^{23}R^{24}$, may be prepared by ortho-lithiation of a compound of formula II wherein $A_1$, $A_2$, $LG_1$, $LG_2$, D, E, M, $L_1$, $L_2$, n and m are as defined for a compound of formula II and K represents hydrogen, followed by reaction with a compound of formula Vc

$$A_3{=}LG_3$$

(Vc)

wherein $A_3$ is as defined for a compound of formula IX and $LG_3$ represents oxygen or $NR^{23}R^{24}$. Preferably, when employing a compound of formula II to synthesise a compound of formula IX, $LG_1$ and $LG_2$ do not represent hydroxyl, as the hydroxyl functionality will typically

have to be protected prior to performing the ortho-lithiation reaction. Preferably, both $LG_1$ and $LG_2$ represent $NR^{23}R^{24}$, most preferably both $LG_1$ and $LG_2$ represent $NMe_2$.

Similarly, a compound of formula I wherein K represents $-A_3-Q^3(X^5)X^6$ and D represents $-A_4-Q^4(X^7)X^8$ may be prepared from a compound of formula IX wherein $A_1$, $A_2$, $A_3$, $LG_1$, $LG_2$, $LG_3$, E, M, $L_1$, $L_2$, n and m are as defined for a compound of formula IX and D represents hydrogen, by sequential ortho-lithiation and reaction with a compound of formula V(d)

$$A_4{=}LG_4$$

(Vd)

wherein $A_4$ is as defined for a compound of formula I and $LG_4$ represents oxygen or $NR^{23}R^{24}$ as defined herein, to form a compound of formula X followed by reaction of the resultant compound of formula X with a phosphine, arsine or stilbene derivative of formula IIIa, IIIb, IIIc as defined herein and a compound of formula IIId

$$HQ^4(X^7)X^8$$

(IIId)

wherein $X^7$ represents $CR^{31}(R^{32})R^{33}$ or adamantyl, $X^8$ represents $CR^{34}(R^{35})(R^{36})$ or adamantyl, or $X^7$ and $X^8$ together with $Q^4$ form a 2-phospha-adamantyl group, or $X^7$ and $X^8$ together with $Q^4$ forms a ring system of formula Id, and $R^{31}$ to $R^{36}$, adamantyl, $Q^4$, 2-phospha-adamantyl, and the ring system of formula Id are as defined for a compound of formula I.

Preferably, when the compound of formula IIIa represents $HQ^2(CR^1(R^2)(R^3))CR^4(R^5)(R^6)$, then the compound of formula IIIb represents $HQ^1(CR^7(R^8)(R^9))CR^{10}(R^{11})(R^{12})$, the compound of formula IIIc represents $HQ^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$ and the compound of formula IIId represents $HQ^4(CR^{31}(R^{32})(R^{33}))CR^{34}(R^{35})(R^{36})$, and $Q^1$ is the same as $Q^2$, $Q^3$ and $Q^4$, $R^1$ is the same as $R^7$, $R^{13}$ and $R^{31}$, $R^2$ is the same as $R^8$, $R^{14}$ and $R^{32}$, $R^3$ is the same as $R^9$, $R^{15}$ and $R^{33}$, $R^4$ is the same as $R^{10}$, $R^{16}$ and $R^{34}$, $R^5$ is the same as $R^{11}$, $R^{17}$ and $R^{35}$, and $R^6$ is the same as $R^{12}$, $R^{18}$ and $R^{36}$.

Preferably, when $X^1$ and $X^2$ in the compound of formula IIIa independently represent adamantyl, then $X^3$ and $X^4$ in the compound of formula IIIb independently represent adamantyl, $X^5$ and $X^6$ in the compound of formula IIIc independently represent adamantyl, and $X^7$ and $X^8$ in the compound of formula IIId independently represent adamantyl.

Preferably, when $X^1$ and $X^2$ together with $Q^2$ to which they are attached in the compound of formula IIIa form a 2-phospha-adamantyl group, then $X^3$ and $X^4$ together with $Q^1$ in the compound of formula IIIb, $X^5$ and $X^6$ together with $Q^3$ in the compound of formula IIIc, and $X^7$ and $X^8$ together with $Q^4$ in the compound of formula IIId each independently form a 2-phospha-adamantyl group.

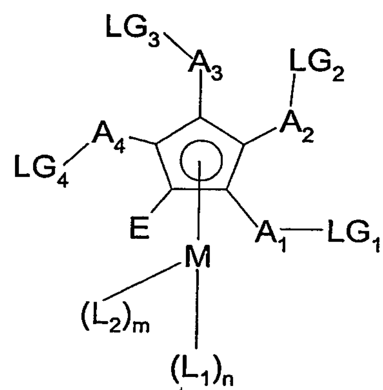
Preferably, when $X^1$ and $X^2$ together with $Q^2$ to which they are attached in the compound of formula IIIa forms a ring system of formula Ia, then $X^3$ and $X^4$ together with $Q^1$ in a compound of formula IIIb, $X^5$ and $X^6$ together with $Q^3$ in a compound of formula IIIc, and $X^7$ and $X^8$ together with $Q^4$ in

a compound of formula IIId, form a ring system of formula Ib, Ic and Id, respectively.

Most preferably, the compounds of formula IIIa, IIIb, IIIc and IIId are identical.

Suitably, when preparing the 1,2,3,4-substituted derivative of the compound of formula I, preferably $LG_1$, $LG_2$ and $LG_3$ of the compound of formula IX do not represent hydroxyl, but each represents $NR^{23}R^{24}$ as defined herein.

Similarly, a compound of formula I wherein K represents $-A_3-Q^3(X^5)X^6$, D represents $-A_4-Q^4(X^7)X^8$, and E represents $-A_5-Q^5(X^9)X^{10}$ may be prepared from a compound of formula XI




(XI)

wherein $A_1$, $A_2$, $A_3$, $LG_1$, $LG_2$, $LG_3$, M, $L_1$, $L_2$, n and m are as defined for a compound of formula IX, $A_4$ is as defined for a compound of formula I, $LG_4$ represents a leaving group, and E represents hydrogen, by sequential ortho-lithiation and reaction with a compound of formula V(e)

$$A_5{=}LG_5$$

(Ve)

wherein $A_5$ is as defined for a compound of formula I and $LG_5$ represents oxygen or $NR^{23}R^{24}$ as defined herein, followed by reaction of the resultant compound with a phosphine, arsine or stilbene derivative of formula IIIa, IIIb, IIIc, IIId as defined herein and formula IIIe

$$HQ^5(X^9)X^{10}$$
(IIIe)

wherein $X^9$ represents $CR^{37}(R^{38})(R^{39})$ or adamantyl, $X^{10}$ represents $CR^{40}(R^{41})(R^{42})$ or adamantyl, or $X^9$ and $X^{10}$ together with $Q^5$ form a 2-phospha-adamantyl group, or $X^9$ and $X^{10}$ together with $Q^5$ form a ring system of formula Ie, and $R^{37}$ to $R^{42}$, adamantyl, 2-phospha-adamantyl, $Q^5$ and the ring system of formula Ie are as defined for a compound of formula I.

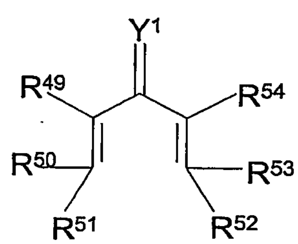
Suitably, when preparing the 1,2,3,4,5-substituted derivative of formula I, preferably $LG_1$, $LG_2$, $LG_3$ and $LG_4$ of the compound of formula X do not represent hydroxyl, but each represents $NR^{23}R^{24}$ as defined herein.

Preferably, the compounds of formula IIIa, IIIb, IIIc, IIId and IIIe are identical.

Compounds of formula IIIa wherein $X^1$ and $X^2$ together with $Q^2$ to which they are attached form a 2-phospha-adamantyl group are obtainable from Cytec Canada Inc of 901 Garner Road, Niagara Falls, Ontario, Canada L2E 6T4. Likewise corresponding 2-phospha-adamantyl compounds of formula IIIb, IIIc, IIId and IIIe may be obtained from the same supplier.

Compounds of formula IIIa where $X^1$ and $X^2$ represent adamantyl may be prepared by methods well known to those skilled in the art, for example by reacting adamantane (or substituted derivative thereof as defined herein) with phosphorous trichloride and aluminium chloride, followed by reduction of the intermediate (adamantyl)$_2$-P(O)Cl derivative. Likewise corresponding compounds of formula IIIb, IIIc, IIId and IIIe where $X^2$ to $X^{10}$ respectively represent adamantyl may be prepared by analogous methods.

Compounds of formula IIIa where $X^1$ and $X^2$ together with $Q^2$ to which they are attached form a ring system of formula Ia may be prepared by reacting a phosphine, arsine or stilbene with a compound of formula XII

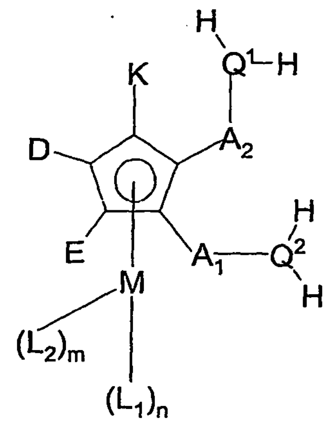


(XII)

where $Y^1$ and $R^{49}$ to $R^{55}$ are as defined for a compound of formula I. Corresponding compounds of formula IIIb, IIIc, IIId and IIIe may be synthesised by analogous methods.

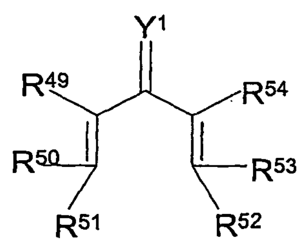
Conveniently, a compound of formula I wherein K, D, E, M, $A_2$, $A_1$, $L_2$, $L_1$, $Q^1$, $Q^2$, m and n are as defined for a compound of formula I and $X^1$ and $X^2$ together with $Q^2$ to which they are attached form a ring system of formula Ia and $X^3$ and $X^4$ together with $Q^1$ to which they are attached

form a ring system of formula Ib, may be formed by reacting a compound of formula XV

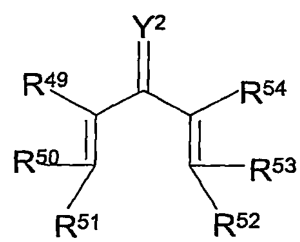


(XV)

wherein K, D, E, M, $A_2$, $A_1$, $L_2$, $L_1$, $Q^1$, $Q^2$, m and n are as defined for a compound of formula I, with a compound of formula XVIa and XVIb



(XVIa)



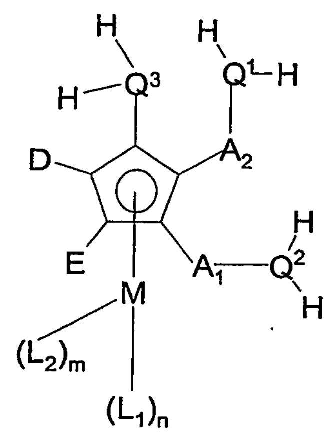
(XVIb)

wherein $Y^1$, $Y^2$, $R^{49}$ to $R^{55}$ are as defined for a compound of formula I.

Suitably, the reaction may be accomplished by heating the reactants at 120°C for approximately 20 hours.

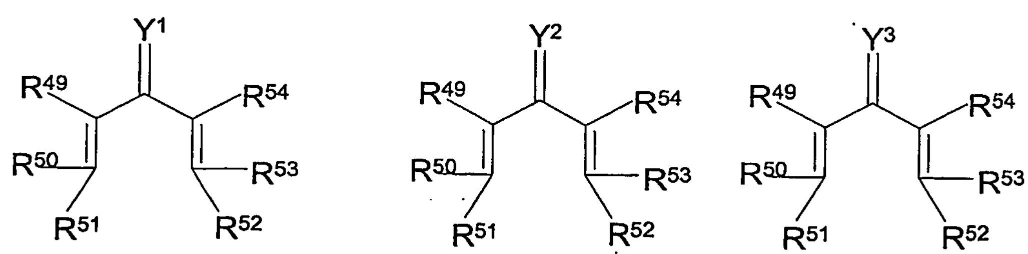
Thus according to a fifth aspect, the present invention provides a compound of formula XV as defined herein.

Similarly, a compound of formula I wherein D, E, M, $A_2$, $A_1$, $L_2$, $L_1$, $Q^1$, $Q^2$, m and n are as defined for a compound of formula I, $X^1$ and $X^2$ together with $Q^2$ to which they are attached form a ring system of formula Ia, $X^3$ and $X^4$ together with $Q^1$ to which they are attached form a ring system of formula Ib, and K represents $-A_3-Q^3(X^5)X^6$ wherein $X^5$ and $X^6$ together with $Q^3$ to which it is attached form a ring system of formula Ic and $A_3$ is as defined for a compound of formula I, may be formed by reacting a compound of formula XVII



(XVII)

wherein D, E, M, $A_2$, $A_1$, M, $L_2$, $L_1$, $Q^1$, $Q^2$, $Q^3$, m and n are as defined for a compound of formula I, with a compound of formula XVIa, XVIb, XVIc

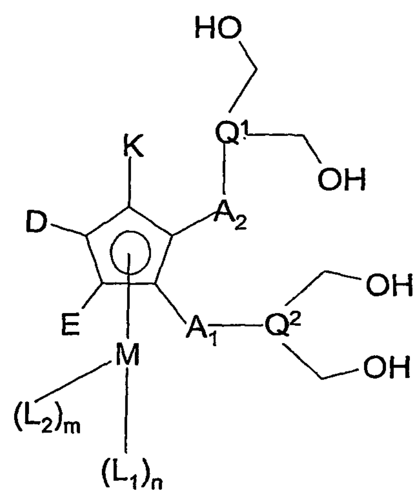


(XVIa) (XVIb) (XVIc)

wherein $Y^1$, $Y^2$, $Y^3$, $R^{49}$ to $R^{55}$ are as defined for a compound of formula I.

Preferably, $Y^1$ is the same as $Y^2$ and $Y^3$ in a compound of formula XVIa, XVIb and XVIc. Most preferably, the compounds of formula XVIa, XVIb and XVIc are identical.

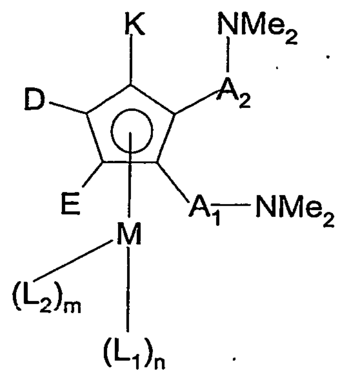
Suitably, the compound of formula XV may be prepared from a compound of formula XVIII, where K, D, E, M, $L_2$, $L_1$, $A_1$, $A_2$, $Q^1$, $Q^2$, n and m are as defined for a compound of formula XV,



(XVIII)

by reduction with for example, sodium metabisufite.

Suitably the compound of formula XVIII may be prepared from a compound of formula XIX wherein K, D, E, M, $A_2$, $A_1$, $L_2$, $L_1$, m and n are as defined for a compound of formula XVIII



(XIX)

by reaction with an alkyl iodide, such as methyl iodide, to form the 1,2-bis-methyl iodide salt derivative of the compound of formula XIX followed by reaction with tris-hydroxymethyl phosphine/stilbene/arsine.

It will be appreciated by those skilled in the art that 1, 2, 3, 4 and 1, 2, 3, 4, 5 substituted compounds may be prepared by analogous methods.

The compounds of formula IIIa, IIIb, IIIc, IIId, IIIe, Va, Vb, Vc, Vd, Ve, VIII, XV, XVIa, XVIb, XVIc, XVII, XIX and derivatives thereof, when neither commercially available nor subsequently described, may be obtained using conventional synthetic procedures in accordance with standard text books on organic chemistry or literature precedent, from readily accessible starting materials using appropriate reagents and reaction conditions.

It will be appreciated by those skilled in the art that, within certain of the processes described, the order of the synthetic steps employed may be varied and will depend *inter alia* on factors such as the nature of other functional groups present in a particular substrate, the availability of key intermediates and the protecting group

strategy (if any) to be adopted. Clearly, such factors will also influence the choice of reagent for use in the said synthetic steps.

It will also be appreciated that various standard substituents or functional group interconversions and transformations within certain compounds of formula I will provide other compounds of formula I.

According to a sixth aspect, the present invention provides a process for the carbonylation of an ethylenically unsaturated compound comprising contacting an ethylenically unsaturated compound with carbon monoxide and a coreactant in the presence of a compound of the present invention.

Suitable coreactants include compounds comprising a nucleophilic moiety and a mobile hydrogen atom. Thus the compounds of the invention may catalyse hydroformylation, hydrocarboxylation, hydroesterification and hydroamidation reactions of an ethylenically unsaturated compound.

Preferred coreactants include molecular hydrogen, water, alcohols, primary or secondary amines or amides, such as diethylamine, N,N-dimethylethylene diamine, carboxylic acids for example acetic acid and pivalic acid, and aromatic alcohols.

Preferably, the coreactant has a hydroxyl functional group or is molecular hydrogen. The hydroxyl containing compounds may be branched or linear, and comprises an alkanol, particularly a $C_1$-$C_{30}$ alkanol, such as neopentyl alcohol, ethylhexyl alcohol, tert-amyl alcohol, including

aryl-alkanols, which may be optionally substituted with one or more substitutents selected from lower alkyl, aryl, Het, halo, cyano, nitro, $OR^{19}$, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $C(S)R^{27}R^{28}$, $SR^{29}$ or $C(O)SR^{30}$ as defined herein. Highly preferred alkanols are $C_1$-$C_8$ alkanols such as methanol, ethanol, propanol, iso-propanol, iso-butanol, t-butyl alcohol, n-butanol, octanol, phenol and chlorocapryl alcohol. Although the monoalkanols are most preferred, polyalkanols, preferably, selected from di-octanols such as diols, triols, tetra-ols and sugars are also possible. Typically, such polyalkanols are selected from 1,2-ethanediol, 1,3-propanediol, glycerol, 1,2,4 butanetriol, 2-(hydroxymethyl)-1,3-propanediol, 1,2,6 trihydroxyhexane, pentaerythritol, 1,1,1 tri(hydroxymethyl)ethane, nannose, sorbase, galactose and other sugars. Preferred sugars include sucrose, fructose and glucose. Especially preferred alkanols are methanol and ethanol.

The amount of alcohol is not critical. Generally, amounts are used in excess of the amount of ethylenically unsaturated compound to be carbonylated. Thus the alcohol may serve as the reaction solvent as well, although, if desired, separate solvents may also be used.

It will be appreciated that the end product of the reaction is determined at least in part by the source of coreactant compound used. If water is used as the hydroxyl group containing compound then the end product is the corresponding carboxylic acid, whereas use of an alkanol produces the corresponding ester.

Preferably, the ethylenically unsaturated compound includes from 2 to 20 carbon atoms. More preferably, the ethylenically unsaturated compound includes 2 to 14 carbon atoms.

Suitably, the ethylenically unsaturated compound may include more than one carbon-carbon double bond, wherein the double bonds are conjugated or non-conjugated.

Preferably, the ethylenically unsaturated compound has 1 to 3 carbon-carbon double bonds per molecule, particularly 1 to 2 carbon-carbon double bonds, especially only 1 carbon-carbon double bond per molecule.

Unless otherwise specified, the ethylenically unsaturated compound may, when there are a sufficient number of carbon atoms, be linear or branched, be cyclic, acyclic or part cyclic/acyclic, and/or be substituted or terminated by one or more substituents selected from lower alkyl, aryl, alkylaryl, Het, alkylHet, halo, $OR^{19}$, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $NO_2$, CN, $SR^{27}$ wherein $R^{19}$ to $R^{27}$ each independently represent hydrogen or lower alkyl. Olefins thus substituted include styrene and alkyl esters of unsaturated carboxylic acids, such as methacrylate. Suitably, the ethylenically unsaturated compound may exhibit cis (E) and trans (Z) isomerism.

Examples of suitable ethylenically unsaturated compounds having 2 or more carbon atoms include ethene, propene, but-1-ene, but-2-ene, isobutene, pentenes, hexenes, octenes, dodecenes, 1,5-cyclooctadiene, cyclododecene, methyl pentenoate, pentene nitrile, 1,3 butadiene, 1,3

pentadiene and 1,3, hexadiene. A particularly preferred ethylenically unsaturated compound is ethene.

The process according to the invention may be especially advantageous for the carbonylation of ethylenically unsaturated compounds which are internally unsaturated, such as but-2-ene or methyl pent-3-enoate. For these compounds side reactions typically occur more readily and linear products may be more difficult to obtain. Conveniently, the compounds of the invention may permit high regioselectivity towards a linear product following carbonylation of internally unsaturated ethylenic compounds.

Preferably, the carbonylation process is carried out at a temperature of from 0°C to 250°C, more preferably 40°C to 150°C, most preferably 70°C to 120°C.

Suitably, the carbonylation process is typically carried out at a pressure of at least atmospheric pressure. Preferably, the carbonylation process is performed under a total pressure of greater than or equal to $1 \times 10^5 Nm^{-2}$, more preferably greater than or equal to $5 \times 10^5 Nm^{-2}$, most preferably greater than or equal to $10 \times 10^5 Nm^{-2}$. Preferably, the carbonylation process is performed under a total pressure of less than or equal to $100 \times 10^5 Nm^{-2}$, more preferably less than or equal to $65 \times 10^5 Nm^{-2}$, most preferably less than or equal to $50 \times 10^5 Nm^{-2}$.

Carbon monoxide partial pressures in the range of 1 to 65, particularly 5 to $50 \times 10^5 Nm^{-2}$, are preferred. In the process according to the present invention, the carbon monoxide may be used in pure form or diluted with an inert

gas such as nitrogen, carbon dioxide or a noble gas such as argon. Small amounts of hydrogen, typically less than 5% by volume, may also be present.

The ratio (volume/volume) of ethylenically unsaturated compound to coreactant containing compound may vary between wide limits and suitably lies in the range of 1:0.1 to 1:10, preferably from 2:1 to 1:2.

The amount of the catalyst of the invention used in the carbonylation process of the ethylenically unsaturated compound is not critical. Good results may be obtained by using $10^{-7}$ to $10^{-1}$ moles, more preferably $10^{-6}$ to $10^{-2}$ moles, of Group VIIIB metal or a compound thereof (referred to as (a) herein) per mole of ethylenically unsaturated compound.

Preferably, as mentioned herein, the process is performed by the inclusion of a source of anions as defined herein in addition to the compounds of the invention. Suitably, a source of anions separate from the compounds of the invention may be added to the carbonylation process. Preferably, as mentioned herein, the compounds of the invention include a source of anions. Suitably, the mole ratio of anions to the moles of Group VIIIB metal in the compounds of the invention when used to carbonylate ethylenically unsaturated compounds lies between wide limits and suitably lies between 2:1 to 2000:1, preferably 5:1 to 500:1, more preferably 10:1 to 200:1.

Suitably, the carbonylation of an ethylenically unsaturated compound as defined herein may be performed in one or more aprotic solvents. Suitable solvents include

ketones, such as for example methylbutylketone; ethers, such as for example anisole (methyl phenyl ether), 2,5,8-trioxanonane (diglyme), diethylether, tetrahydrofuran, diphenylether, diisopropylether and the dimethylether of di-ethylene-glycol; esters, such as for example methylacetate, dimethyladipate and butyrolactone; amides, such as for example dimethylacetamide and N-methylpyrrolidone; and sulfoxides and sulphones, such as for example dimethylsulphoxide, di-isopropylsulphone, sulfolane (tetrahydrothiophene-2,2-dioxide) 2-methylsulfolane and 2-methyl-4-ethylsulfolane.

Very suitable are aprotic solvents having a dielectric constant that is below a value of 50, more preferably in the range of 3 to 8, at 298.15 K and 1 x $10^5 Nm^{-2}$. In the present context, the dielectric constant for a given solvent is used in its normal meaning of representing the ratio of the capacity of a condenser with that substance as dielectric to the capacity of the same condenser with a vacuum for dielectric. Values for the dielectric constants of common organic liquids can be found in general reference books, such as the Handbook of Chemistry and Physics, 76$^{th}$ edition, edited by David R. Lide et al, and published by CRC press in 1995, and are usually quoted for a temperature of about 20°C or 25°C, i.e. about 293.15k or 298.15 K, and atmospheric pressure, i.e. about 1 x $10^5 Nm^{-2}$, or can readily be converted to that temperature and pressure using the conversion factors quoted. If no literature data for a particular compound is available, the dielectric constant may be readily measured using established physico-chemical methods.

For example, the dielectric constant of anisole is 4.3 (at 294.2 K), of diethyl ether is 4.3 (at 293.2 K), of sulfolane is 43.4 (at 303.2 K), of methylpentanoate is 5.0 (at 293.2 K), of diphenylether is 3.7 (at 283.2 K), of dimethyladipate is 6.8 (at 293.2 K), of tetrahydrofuran is 7.5 (at 295.2 K), of methylnonanoate is 3.9 (at 293.2 K). A preferred solvent is anisole.

If the coreactant compound is an alkanol, a further preferred aprotic solvent is the ester carbonylation product of the ethylenically unsaturated compound, carbon monoxide and the alkanol.

The process may advantageously be carried out in an excess of aprotic solvent, i.e. at a ratio (v/v) of aprotic solvent to coreactant containing compound of at least 1:1. Preferably, this ratio ranges from 1:1 to 10:1 and more preferably from 1:1 to 5:1. Most preferably the ratio (v/v) ranges from 1.5:1 to 3:1.

The catalyst compounds of the present invention may act as a "heterogeneous" catalyst or a "homogeneous" catalyst.

By the term "homogeneous" catalyst we mean a catalyst, i.e. a compound of the invention, which is not supported but is simply admixed or formed in-situ with the reactants of the carbonylation reaction (e.g. the ethylenically unsaturated compound, the hydroxyl containing compound and carbon monoxide), preferably in a suitable solvent as described herein.

By the term "heterogeneous" catalyst we mean a catalyst, i.e. the compound of the invention, which is carried on a support.

Thus according to a seventh aspect, the present invention provides a catalyst system comprising a support, preferably an insoluble support, and a compound of the invention as defined herein. Conveniently, the use of an insoluble support permits easy separation of the catalyst, for example by filtration, from the reaction medium.

Preferably, the support comprises a polymer such as a polyolefin, polystyrene and polystyrene/divinylbenezene copolymer; a silicon derivative such as a functionalised silica, a silicone or a silicone rubber; or other porous particulate material such as for example inorganic oxides and inorganic chlorides such as alumina and montmorillomite.

Preferably the support material is porous silica which has a surface area in the range of from 10 to 700 $m^2/g$, a total pore volume in the range of from 0.1 to 4.0 cc/g and an average particle size in the range of from 10 to 500$\mu m$. More preferably, the surface area is in the range of from 50 to 500 $m^2/g$, the pore volume is in the range of from 0.5 to 2.5 cc/g and the average particle size is in the range of from 20 to 200 $\mu m$. Most desirably the surface area is in the range of from 100 to 400 $m^2/g$, the pore volume is in the range of from 0.8 to 3.0 cc/g and the average particle size is in the range of from 30 to 100 $\mu m$. The average pore size of typical porous support materials is in the range of from 10 to 1000 Å. Preferably, a support material is used that has an average

pore diameter of from 50 to 500 Å, and most desirably from 75 to 350 Å. It may be particularly desirable to dehydrate the silica at a temperature of from 100°C to 800°C anywhere from 3 to 24 hours.

Suitably, the support may be flexible or a rigid support, the insoluble support is coated and/or impregnated with the compound of the invention by techniques well known to those skilled in the art. Alternatively, the compound of the invention is fixed to the surface of insoluble support, optionally via a covalent bond, and optionally includes a bifunctional spacer molecule to space the compound from the insoluble support.

The compounds of the invention may be fixed to the surface of the insoluble support by promoting reaction of a functional group present in the compound of formula I, for example a substituent of the ligand $L_1$ or a substituent K, D and E of the cyclopentadienyl moiety, with a complimentary reactive group present on or previously inserted into the support. The combination of the reactive group of the support with a complimentary substituent of the compound of the invention provides a heterogeneous catalyst where the compound of the invention and the support are linked via a linkage such as an ether, ester, amide, amine, urea, keto group.

The choice of reaction conditions to link a compound of the present invention to the support depend upon the nature of the substituents(s) of the compound and the groups of the support. For example, reagents such as carbodiimides, 1,1′-carbonyldiimidazole, and processes

such as the use of mixed anhydrides, reductive animation may be employed.

According to an eighth aspect, the present invention provides the use of a compound of the invention or a compound of the invention attached to a support as a catalyst.

It will be appreciated that any of the features set forth in the first aspect of the invention may be regarded as preferred features of the second, third, fourth, fifth, sixth, seventh and eighth aspect of the present invention and vice versa.

The invention will now be described by way of the following non-limiting examples.

Example 1

Preparation of 1,2-bis-(dimethylaminomethyl)ferrocene

n-Butyllithium (Aldrich, 2.5 molar in hexane, 24 ml, 54 mmol) is added to a solution of (dimethylaminomethyl)ferrocene (Aldrich, 13.13 g, 10.69 ml, 48.97 mmol) in diethyl ether (80 ml) under nitrogen at a temperature of 25°C and the reaction mixture stirred for 4 hours. The resulting red solution is then cooled to approximately -70°C in a dry ice/acetone bath and Eschenmosers salt ($ICH_2NMe_2$) (Aldrich, 10 g, 54 mmol) is added. The reaction is allowed to warm to room temperature and stirred overnight.

The resultant solution is quenched with excess aqueous sodium hydroxide and the resulting product extracted with

diethyl ether (3 x 80 ml) dried over anhydrous magnesium sulfate, filtered over celite, and volatiles removed *in vacuo* to yield the crude title compound as a light orange crystalline solid. The crude product is recrystallised from light petrol with cooling to -17°C and the recrystallised product washed with cold petrol to yield the title compound as a light orange solid (13.2 g, 74%). The compound can be further purified by sublimation to give 8.5 g (52%) of the title compound (mpt 74°C).

$^1$H NMR(250 MHz; $CDCl_3$):δ4.23(brd, 2H); 4.11-4.10(t, 1H); 4.04(s, 5H); 3.43, 3.38, 3.23, 3.18 (AB quartet, 2H); 2.22(s, 6H).

$^{13}$C NMR (63 MHz; $CDCl_3$):δ83.81; 70.40; 69.25; 66.84; 57.35; 45.23.

| | | | | |
|---|---|---|---|---|
| Elemental analysis: | Found: | C 63.7%; | H 8.9%; | N 9.5% |
| | Calculated: | C 64.0%; | H 8.1%; | N 9.4% |

Example 2

Preparation of 1,2-bis-(ditertbutylphosphinomethyl)ferrocene

Di-tertbutylphosphine (Aldrich, 0.616 ml, 3.33 mmol) was added to a solution of 1,2-bis(dimethylaminomethyl)ferrocene (Example 1, 0.5 g, 1.66 mmol) in anhydrous acetic acid (100 ml) under nitrogen and the resulting mixture is stirred at 80°C for 72 hours. The anhydrous acetic acid is removed *in vacuo* at approximately 70°C to yield the crude title product as an orange/yellow solid. The crude product is recrystallised from ethanol with cooling to -17°C, filtered and the filtrate washed

with cold ethanol to yield the title compound as a pale yellow solid (0.365 g, 44%, 84°C).

$^{1}H$ NMR (250 MHz; $CDCl_3$): δ4.4 (2H, d, J = 2Hz); 3.95(5H, s); 3.75 (1H, t, 2Hz); 2.8 (2H, dd, 12Hz, 2Hz); 2.6 (2H, dd, 12Hz, 2Hz); 1.1 (18H, m).

$^{13}C$ NMR (63 MHz; $CDCl_3$): δ86.73 (d, 5.46 Hz); 70.08 (d, 4.41 Hz); 69.4665(s); 63.75(s); 31.80 (d, 2Hz); 31.45 (d, 1.98Hz); 29.89 (d, 1.88 Hz).

$^{31}P$ NMR (101 MHz; $CDCl_3$): δ15.00 ppm.

Elemental analysis: Found: C:66.79%; H:9.57%
Calculated: C:66.93%; H:9.63%

<u>Example 3</u>

<u>Preparation of 1-hydroxymethyl-2-dimethylaminomethyl ferrocene</u>

n-Butyl lithium (Aldrich, 1.6 molar in diethyl ether, 5.14 ml, 8.24 mmol) is added to a solution of 1-dimethylaminomethyl ferrocene (Aldrich, 1.0g, 4.12mmol) in diethyl ether (20mL) under argon. The reaction is stirred for 3 hours and developes a reddish colour. The solution is then cooled in a dry ice/acetone bath, calcined para-formaldehyde (0.247g, 2 times excess) added and the resultant mixture stirred overnight at room temperature. The reaction is then quenched with water, extracted with diethyl ether, dried over $MgSO_4$, and filtered over celite. The solvent is removed *in vacuo* to yield crude title compound. The crude product is applied to a neutral alumina column, which is eluted with petrol/diethyl ether

(9:1 ratio) to remove the starting material, 1-dimethylaminomethyl ferrocene. The column is then eluted with substantially pure ethyl acetate to elute the title compound. The ethyl acetate is removed *in vacuo*, to yield the title compound as an orange oil/crystalline mass.

$^1$H NMR (250 MHz; $CDCl_3$) δ2.131 (s, 6 H), δ2.735 (d, 1 H, 12.512 Hz), δ3.853 (d, 1 H, 12.512 Hz), δ3.984 (dd, 1 H, 2.156 Hz), δ4.035 (s, 5 H), δ4.060 (dd, 1 H, 2.136 Hz) δ4.071 (d, 1 H, 12.207 Hz), δ4.154 (m, 1 H), δ4.73 (d, 1 H, 12.207 Hz).

$^{13}$C NMR (61 MHz; $CDCl_3$) δ7.688, δ84.519, δ70.615, δ68.871, δ68.447, δ65.369, δ60.077, δ58.318, δ44.414

COSY 2D $^1$H NMR
Partly obscured doublet at 4.071ppm and its coupling to the doublet at 4.73 ppm confirmed.
Infrared spectra ($CHCl_3$) (c.a. 0.06g / 0.8mL)
2953.8 $cm^{-1}$ , 2860.6 $cm^{-1}$, 2826.0 $cm^{-1}$, 2783.4 $cm^{-1}$, 1104.9 $cm^{-1}$

Example 4
Preparation of 1,2-bis-(ditertbutylphosphinomethyl)ferrocene

Di-tertbutylphosphine (Aldrich, 0.54 ml, 2.93 mmol) is added to a solution of 1-hydroxymethyl-2-dimethylaminomethyl ferrocene (Example 3, 0.2 g, 0.753 mmol) in anhydrous acetic acid (15 ml) and acetic anhydride (0.753 mmol) under argon and the resulting mixture is stirred at 80°C for 72 hours. The anhydrous acetic acid is removed *in vacuo* at approximately 70°C to

yield the crude title product as an orange/yellow solid. The crude product is recrystallised from ethanol with cooling to −17°C, filtered and the filtrate washed with cold ethanol to yield the title compound as an orange solid (0.23 g)

$^1H$ NMR (250 MHz; $CDCl_3$) δ4.351 (d, 2 H, 2Hz), δ4.022 (s, 5 H), δ3.827 (t, 1 H, 2 Hz), δ2.858 (ddd, 2 H, $J_{HH}$ 15.869 Hz, $J_{HP1}$ 3.320 Hz, $J_{HP2}$ 1.831 Hz), δ2.679 (dd, 2 H, $J_{HH}$ 15.869 Hz, $J_{HP}$ 2.441 Hz), δ1.166 (d, 18 H, 12.817 Hz), δ1.123 (d, 18 H, 12.512 Hz)

FTIR (Chloroform, NaCl plates)
1104.1 $cm^{-1}$, 2863$cm^{-1}$, 2896.0 $cm^{-1}$, 2940.0 $cm^{-1}$, 2951.8 $cm^{-1}$

Elemental analysis: Found: C:66.5%; H:9.6%
Calculated: C:66.9%; H:9.6%

Example 5

Preparation of 1-hydroxymethyl-2,3-bis-(dimethylaminomethyl)ferrocene

To a stirred solution of 1,2-bis-(dimethylaminomethyl) ferrocene (Example 1, 0.70g, 2.32 mmol) in diethyl ether (15 $cm^3$) under argon is added 1.2 equivalents n-butyl lithium (Aldrich, 1.75mL, 1.6M in diethyl ether) and the mixture stirred for three hours to yield a red solution. The reaction mixture is cooled in a dry ice/acetone bath, calcined paraformaldehyde added in 2:1 excess, and the resultant mixture stirred at room temperature overnight. The mixture is quenched with water and extracted with diethyl ether. The ethereal extracts are dried over $MgSO_4$,

filtered over celite and the solvent removed *in vacuo*, to yield the title compound (0.7g , 2.12 mmol, 91%) as an orange oil., which partially crystallized on cooling.

$^1H$ NMR (250 MHz; $CDCl_3$) δ 2.133 (s, 6 H ), δ 2.171 (s, 6 H), δ 2.910 (d, 1 H, 12.817 Hz), δ 2.998 (d, 1 H, 12.512 Hz), δ 3.425 (d, 1 H, 12.817 Hz), δ 3.812 (d, 1 H, 12.512 Hz), δ 3.962 (s, 5 H), δ 3.99 (d, 1 H, 12.207 Hz) (partly obscured by large cp-ring peak at δ 3.962), δ 4.068 (d, 1 H, δ2.136 Hz), δ 4.125 )d, 1 H, δ 2.136 Hz), δ 4.747 (d, 1 H, 12.207 Hz)

$^{13}C$ NMR (60 MHz; $CDCl_3$) δ44.529, δ45.244, δ55.798, δ57.906, δ60.271, δ67.944, δ68.277, δ69.612, δ84.850, δ88.322

Infrared spectra ($CDCl_3$ / thin film NaCl plates )
3380.6 $cm^{-1}$ (br), 2955.7 $cm^{-1}$ (m), 2862.6 $cm^{-1}$ , 2825.9 $cm^{-1}$ (m), 2774.3 $cm^{-1}$ (m), 1353.5 $cm^{-1}$ (m), 1104.9 $cm^{-1}$ (m), 1038.9 $cm^{-1}$ (m), 1006.8 $cm^{-1}$ (s)

Elemental analysis: Found: C: 62.3%; H: 7.8%; N: 8.8%
Calculated: C:61.8%; H:7.9%; N:8.5%

Example 6

Preparation of 1,2,3-tris-(ditertbutylphosphinomethyl)ferrocene

Di-tert-butylphosphine (Aldrich, 2.60 mL, 13.98 mmol) and acetic anhydride (0.24 mL, 2.33 mmol) is added to a solution of 1-hydroxymethyl-2,3-bis-(dimethylaminomethyl)ferrocene (Example 5, 0.70g, 2.12 mmol) in acetic acid (freshly distilled from acetic

anhydride 25 $cm^3$ ), under argon. The solution is then stirred at 80°C for 7 days, during which time the solution becomes a dark orange colour. The solvent is then removed *in vacuo* and recrystallisation effected from refluxing ethanol together with cooling to –17°C overnight to yield the title compound (0.43 g, 0.7 mmol, 31%) as a yellow/orange powder.

$^1H$ NMR (250 MHz, $CDCl_3$) δ 1.12 (dd - pseudo triplet, 36 H, 12.1 Hz), δ1.26 (d, 18H, 10.7 Hz), δ2.68 (d, 2 H, 17.7 Hz), δ2.95 (s, 2 H), δ3.07, (m, 2 H), δ4.01 (s, 5 H) δ 4.33 (s, 2 H)

Infrared spectra ($CHCl_3$ / thin film NaCl plates )
1365.5 $cm^{-1}$, 1470.3 $cm^{-1}$ , 2357.1 $cm^{-1}$ ,2862.8 $cm^{-1}$ , 2896.7 $cm^{-1}$ , 2939.1 $cm^{-1}$

Example 7

Preparation of 1,2-bis-(diadamantylphosphinomethyl)ferrocene-bis-methanesulphonate

Di-adamantylphosphine (prepared according to J.R.Goerlich, R.Schmutzler; Phosphorus Sulphur and Silicon; 1995, 102, 211-215, 20.0g, 0.066 mol) was added to a solution of 1,2-bis(dimethylaminomethyl)ferrocene (Example 1, 10 g, 0.033 mol) in anhydrous acetic acid (100 ml) under nitrogen and the resulting mixture is stirred at 80°C for 72 hours. The orange yellow precipitate which forms is filtered and dried *in vacuo* at approximately 70°C to yield the title compound as an orange/yellow solid. The title compound is insoluble in a range of organic solvents and it is therefore purified by conversion to the bis-

methanesulphonate salt by addition of excess methanesulphonic acid to a methanol slurry of the crude product. This resulted in complete dissolution of the product salt which was then isolated by removal of the methanol *in vacuo* followed by washing with ether and drying to give the title compound as a pale yellow solid (14.0g, 54%).

$^1$H NMR (250 MHz; $CD_3CN$): δ4.57 (2H, d, J = 2Hz); 4.35 (5H, s); 4.27 (1H, t, 2Hz); 3.34 (4H, br); 2.6 (6H, br,); 2.35-2.18 (18H br); 2.16-2.0 (18H, br); 1.92-1.72 (24H, br).

$^{31}$P NMR (101 MHz; $CD_3CN$): δ26.58 ppm.

Elemental analysis: Found: C:64.15%; H:7.88% Calculated: C:64.29%; H:7.94%

Example 8

Preparation of 1,2-bis-(di-(1,3,5-trimethyl-6,9,10-trioxa-adamantylphosphinomethyl))ferrocene

1,3,5,trimethyl-2,4,8-trioxa-6-phospha-adamantane (obtained from Cytec, 14.0g, 0.066 mol) was added to a solution of 1,2-bis(dimethylaminomethyl)ferrocene (Example 1, 10 g, 0.033 mol) in anhydrous acetic acid (100 ml) under nitrogen and the resulting mixture is stirred at 80°C for 72 hours. The anhydrous acetic acid is removed *in vacuo* at approximately 70°C to yield the crude title product as an orange/yellow solid. This is washed with hot methanol to give the product as a mixture of isomers as an orange solid. (12.0g, 58%).

$^1H$ NMR (250 MHz; $CDCl_3$): δ4.25-3.95 (8H, br, m); 3.46 (4H, br); 1.57-2.0 (8H, br, m); 1.43-1.23 (24H, br m).

$^{31}P$ NMR (101 MHz; $CDCl_3$): δ -27.41 (br), -29.01 (s), -33.9 (br) ppm.

Elemental analysis: Found: C:57.80%; H:7.35% Calculated: C:57.87%; H:7.40%

Example 9

Preparation of 1,2-bis-(dimethylaminomethyl)ferrocence-bis methyl iodide

Methyl iodide (23.28g, 0.164 mol) is added to a solution of 1,2-bis-(dimethylaminomethyl)ferrocence (Example 1, 20g, 0.082 mol) in degassed methanol (100 ml), and the mixture stirred at room temperature under a nitrogen atmosphere for 24 hours. The resulting precipitate is removed by filtration, washed with ether and dried to yield the title compound (43.0g).

Elemental analysis: Found: C:36.8%; H:5.1%; N,4.8%
Calculated: C:37.0%; H:5.2%; N,4.8%

$^{13}C$ NMR ($D_2O$): δ53.27, δ53.21, δ53.15, δ64.68, δ71.77, δ73.24, δ74.13, δ74.95

Example 10

Preparation of 1,2-bis(dihydroxymethylphosphinomethyl) ferrocene

Potassium hydroxide (8.52g, 0.152 mol) is added to a solution of tetrakis(hydroxymethyl) phosphonium chloride

(Aldrich, 38.54g of 80% w/w aqueous solution, 0.162 mol) in degassed methanol (40 ml), and stirred at room temperature under a nitrogen atmosphere for 1 hour. The resultant mixture is added dropwise to a degassed solution of 1,2-bis-(dimethylaminomethyl)ferrocene-bis-methyl iodide (Example 9, 19.98g, 52.2 mmol) in methanol (40 ml) under nitrogen at room temperature with stirring. The resultant mixture is refluxed under nitrogen for 20 hours, and the solvent removed in vacuo to form a red precipitate. Water (30 ml), diethyl ether (85 ml) and triethylamine (35 ml) is added to the precipitate and the solution stirred at room temperature for 1 hour. The aqueous layer is removed and re-extracted with diethyl ether (2 x 30 ml). The combined ethereal extracts are washed with water (3 x 20 ml) dried over sodium sulphate and filtered. The ether is removed in vacuo to yield the crude title compound (14.33g, 94% yield) as a microcrystalline orange solid. The crude product is recrystallised from a warm dicholormethane/methanol solution with the addition of light petroleum and cooling to yield the title compound (10.69g, 70% yield) as yello-orange crystals.

Elemental analysis: Found: C:48.44%; H:4.12%; N,0.0%
Calculated: C:48.24%; H:4.02%; N,0.0%

$^1H$ NMR: δ1.75 (s, br), δ2.70 (dd, 2 H, $J^2_{HH}$ 14.2 Hz, $J^2_{HP}$ 6.6 Hz), δ2.85 (dd, 2 H, $J^2_{HH}$ 14.2 Hz, $J^2_{HP}$ 7.9 Hz), δ3.71 (t, 1 H, $J_{HH}$ 2.44 Hz), δ3.58 (s, 5 H), δ3.98 (d, 2 H, $J_{HH}$ 2.40 Hz), 4.06 (m, 8 H).

$^{1}H\{^{31}P\}$ NMR: δ1.75 (s, br), δ2.70 (d, 14.3 Hz), δ2.85 (d, 14.3 Hz), δ4.04 (m, 1 H), δ4.06 (s, 8 H), δ4.08 (s, 5H), δ4.1 (m, 2 H)

$^{13}C$ NMR: δ23.7 (d, $J^{1}_{PC}$ 15.6 Hz), δ63.0 (d, $J^{1}_{PC}$ 15.6 Hz), δ66.0 (s), δ67.2 (d, $J^{3}_{PC}$ 9.2 Hz), δ69.6 (s), δ82.6 (d, $J^{2}_{PC}$ 14.7 Hz)

$^{31}P$ NMR: δ-14.7

Infrared spectra ($CHCl_3$ / thin film NaCl plates ) 3337.8 $cm^{-1}$(st, br), further peaks 1104 $cm^{-1}$ 2929.0 $cm^{-1}$, 3603.7 $cm^{-1}$ ,3683.7 $cm^{-1}$.

Example 11

Preparation of 1,2-bis(diphosphinomethyl)ferrocene

1,2-bis(dihydroxymethylphosphinomethyl)ferrocene (Example 10, 5.45g, 13.70 mmol) and sodium metabisulfite (5.21g, 27.4 mmol) is added to a two-phase solvent system consisting of distilled water (60 ml) and light petroleum (60 ml). The mixture is refluxed for 3 hours in air. The resultant mixture is cooled stirred and the aqueous layer removed. The organic layer is washed with distilled water and the organic solvent removed in vacuo to yield the title compound (2.66g, 70% yield) as an orange crystalline solid.

Elemental analysis: Found: C:51.65%; H:5.75%
Calculated: C:51.80%, H:5.76%

$^{1}H$ NMR (250 MHz; $CDCl_3$): δ 2.7-2.8 (m, 4H), δ 3.17 (m, 2H), δ 3.18 (m, 2H), δ 4.04 (t, 1H, J=2.54 Hz), δ 4.09 (d, 5H, $J_{HP}$ 0.4 Hz), δ 4.13 (d, 2H, J=2.54 Hz)

$^{31}P$ NMR (101 MHz; $CDCl_3$): δ 130.0 (t, $J_{HP}$ 193.0 Hz)

$^{13}C$ NMR (60 MHz; $CDCl_3$): δ 12.9, δ 65.6, δ 67.3, δ 69.4, δ 86.9

$^{13}C$ DEPT NMR ($CDCl_3$): δ 12.9 ($CH^2$), δ 65.6 (CH), δ 67.3 (CH), δ 69.40 (5 x CH)

FTIR (Chloroform, NaCl plates): 2298.5 $cm^{-1}$ (strong)

Mass spectrum: Found m/z: 278.0088; Calculated m/z 278.0077

Example 12

Preparation of 1,2-bis-α,α-(P-(2,2,6,6,-tetramethylphosphinan-4-one))dimethylferrocene

2,6-Dimethyl-2,5-heptadiene-4-one (14.6g, 0.106 mol) is added to 1,2-bis-(diphosphinomethyl)ferrocene (Example 11, 14.7g, 0.053 mol) and the mixture heated to 120°C under nitrogen for 20 hours. The reaction mixture is cooled, the crude title compound removed by filtration, washed with pentene (20 ml) and dried in vacuo to yield the title compound as a yellow-orange solid (24.9g, 85% yield). The title compound was characterised by $^{31}P$ NMR and mass spectrum.

Example 13

Preparation of methyl propanoate from ethylene, carbon monoxide and methanol catalysed by a compound of the present invention

A mechanically stirred autoclave (Hastelloy) of 2 litre capacity was evacuated of air and then charged with a solution of tri(dibenzylideneacetone)dipalladium ($1.44 \times 10^{-5}$ moles), 1,2-bis-(di-tertbutylphosphinomethyl) ferrocene of Example 2, ($7.61 \times 10^{-5}$ moles) and methane sulfonic acid ($2.25 \times 10^{-3}$ moles) in 300 ml of methyl propanoate/methanol (70 wt% methyl propanoate). The autoclave was heated to 100°C and when at that temperature, ethylene ($8 \times 10^5 Nm^{-2}$) was added on top of the vapour pressure of the solvents and immediately an equimolar mixture of carbon monoxide and ethylene ($2 \times 10^5 Nm^{-2}$) added to the system through a pressure regulating valve set to $10 \times 10^5 Nm^{-2}$ above the solvent vapour pressure. Suitably, the molar ratio of ethylene to carbon monoxide in the reactor is approximately 9:1. The temperature of the reactor was maintained at 100°C and as the reaction proceeded additional carbon monoxide and ethylene was added (on an equimolar basis) through the pressure regulating Tescom valve. No catalyst precipitation was observed.

Initial reaction rates measured in moles of methyl propanoate (MeP) per mole of palladium per hour and turnover measured in moles of methyl propanoate per mole of palladium were determined for the catalyst. This may be accomplished by an analysis of the amount of gas consumed per unit time (rate) and the total amount of gas consumed

during the reaction, assuming ideal gas behaviour and 100% selectivity to methyl propanoate.

The reaction was repeated (Run 2) and initial reaction rates and turnover numbers calculated as described above. The data for both runs is displayed in Table 1.

| | Maximum (moles MeP/mole Pd/hr) Initial Rate | Turnover (moles MeP/mole Pd/hr) number after 3 hours |
|---|---|---|
| Run 1 | 31,810 | 59,941 |
| Run 2 | 30,322 | 63,941 |

Table 1

Comparative Example 14

Preparation of methyl propanoate from ethylene, carbon monoxide and methanol catalysed by a known catalyst

Example 13 was repeated twice (Runs 3 and 4 respectively) except the catalyst system was as disclosed in WO 96/19434 and obtained by charging the autoclave with tri(dibenzylideneacetone)dipalladium (1.44 x $10^{-5}$ moles), 1,2 bis(di-t-butylphosphinomethyl)benzene (7.61 x $10^{-5}$ moles) and methane sulfonic acid (2.25 x $10^{-3}$ moles) in methyl propanoate/methanol (300 ml, 70 wt% methyl propanoate).

The initial reaction rates (moles MeP/mole Pd per hour) and turnover numbers (moles Pd/moles MeP) for the catalyst were calculated as described in Example 13 above. The results are presented in Table 2 below.

| | Maximum Initial Rate (moles Pd/moles MeP/hr) | Turnover number after 3 hours (moles Pd/mole MeP) |
|---|---|---|
| Run 3 | 29,730 | 48,386 |
| Run 4 | 30,335 | 51,997 |

Table 2

The results demonstrate (see Table 1 and Table 2), that the catalyst of the present invention palladium 1,2-bis-(di-t-butylphosphinomethyl)ferrocene and the known palladium 1,2-bis(di-t-butylphosphinomethyl)benzene exhibit comparable initial catalytic reaction rates. However, the turnover number for the catalyst of the invention is significantly higher than that for the known palladium 1,2-bis(di-t-butylphosphinomethyl)benzene catalyst, thereby indicating that the compound of the present invention increases the rate of the carbonylation reaction compared to the known bidentate system.

Example 15

Preparation of methyl propanoate from ethylene, carbon monoxide and methanol catalysed by a compound of the present invention

Example 13 was repeated (Runs 5 to 9 respectively) except the catalyst system employed was obtained by charging the autoclave with 1,2-bis-(diadamantylphosphinomethyl) ferrocene-bis-methane sulphonate (Example 7, $7.61 \times 10^{-5}$ moles), tri(dibenzylideneacetone)dipalladium ($1.44 \times 10^{-5}$ moles) and methane sulfonic acid ($2.25 \times 10^{-3}$ moles) in methyl propanoate/methanol (300 ml, 70 wt% methyl propanoate).

The initial reaction rates (moles MeP/mole Pd per hour) and turnover numbers (moles Pd/moles MeP) for the catalyst were calculated as described in Example 13 above. The results are presented in Table 3 below.

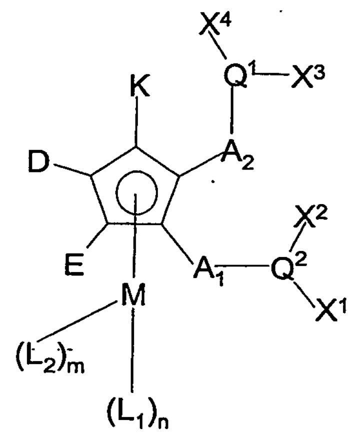
| | Maximum Initial Rate (moles Pd/moles MeP/hr) | Turnover number after 3 hours (moles Pd/mole MeP) |
|---|---|---|
| Run 5 | 52,854 | 67,885 |
| Run 6 | 37,034 | 64,996 |
| Run 7 | 35,986 | 64,441 |
| Run 8 | 40,781 | 62,108 |
| Run 9 | 39,251 | 62,108 |

Table 3

The results demonstrate (see Table 3 and Table 2), that the catalyst of the present invention palladium 1,2-bis(diadamantylphosphinomethyl)ferrocene-bis-methane sulphonated exhibits a significantly higher initial catalytic rate and a significantly higher turnover number than the known catalyst palladium 1,2-bis-(di-t-butylphosphinomethyl)benzene, thereby indicating the compound of the present invention increases the rate of the carbonylation reaction compared to the known bidentate system.

**Claims**

1. A compound obtainable by combining:
   (a) a Group VIIIB metal or a compound thereof; and,
   (b) a compound of formula I or salt thereof:



(I)

wherein:

$A_1$ and $A_2$, and $A_3$, $A_4$ and $A_5$ (when present), each independently represent lower alkylene;

K is selected from the group consisting of hydrogen, lower alkyl, aryl, Het, halo, cyano, nitro, $-OR^{19}$, $-OC(O)R^{20}$, $-C(O)R^{21}$, $-C(O)OR^{22}$, $-N(R^{23})R^{24}$, $-C(O)N(R^{25})R^{26}$, $-C(S)(R^{27})R^{28}$, $-SR^{29}$, $-C(O)SR^{30}$, $-CF_3$ or $-A_3-Q^3(X^5)X^6$;

D is selected from the group consisting of hydrogen, lower alkyl, aryl, Het, halo, cyano, nitro, $-OR^{19}$, $-OC(O)R^{20}$, $-C(O)R^{21}$, $-C(O)OR^{22}$, $-N(R^{23})R^{24}$, $-C(O)N(R^{25})R^{26}$, $-C(S)(R^{27})R^{28}$, $-SR^{29}$, $-C(O)SR^{30}$, $-CF_3$ or $-A_4-Q^4(X^7)X^8$;

E is selected from the group consisting of hydrogen, lower alkyl, aryl, Het, halo, cyano, nitro, $-OR^{19}$, $-OC(O)R^{20}$,

$-C(O)R^{21}$, $-C(O)OR^{22}$, $-N(R^{23})R^{24}$, $-C(O)N(R^{25})R^{26}$, $-C(S)(R^{27})R^{28}$, $-SR^{29}$, $-C(O)SR^{30}$, $-CF_3$ or $-A_5-Q^5(X^9)X^{10}$;

or both D and E together with the carbon atoms of the cyclopentadienyl ring to which they are attached form an optionally substituted phenyl ring:

$X^1$ represents $CR^1(R^2)(R^3)$ or adamantyl, $X^2$ represents $CR^4(R^5)(R^6)$ or adamantyl, or $X^1$ and $X^2$ together with $Q^2$ to which they are attached form an optionally substituted 2-phospha-tricyclo[3.3.1.1{3,7}]decyl group or derivative thereof, or $X^1$ and $X^2$ together with $Q^2$ to which they are attached form a ring system of formula 1a;

$X^3$ represents $CR^7(R^8)(R^9)$ or adamantyl, $X^4$ represents $CR^{10}(R^{11})(R^{12})$ or adamantyl, or $X^3$ and $X^4$ together with $Q^1$ to which they are attached form an optionally substituted 2-phospha-tricyclo[3.3.1.1{3,7}]decyl group or derivative thereof, or $X^3$ and $X^4$ together with $Q^1$ to which they are attached form a ring system of formula 1b;

$X^5$ represents $CR^{13}(R^{14})(R^{15})$ or adamantyl, $X^6$ represents $CR^{16}(R^{17})(R^{18})$ or adamantyl, or $X^5$ and $X^6$ together with $Q^3$ to which they are attached form an optionally substituted 2-phospha-tricyclo[3.3.1.1{3,7}]decyl group or derivative thereof, or $X^5$ and $X^6$ together with $Q^3$ to which they are attached form a ring system of formula 1c;

$X^7$ represents $CR^{31}(R^{32})(R^{33})$ or adamantyl, $X^8$ represents $CR^{34}(R^{35})(R^{36})$ or adamantyl, or $X^7$ and $X^8$ together with $Q^4$ to which they are attached form an optionally substituted 2-phospha-tricyclo[3.3.1.1{3,7}]decyl group or derivative

thereof, or $X^7$ and $X^8$ together with $Q^4$ to which they are attached form a ring system of formula 1d;

$X^9$ represents $CR^{37}(R^{38})(R^{39})$ or adamantyl, $X^{10}$ represents $CR^{40}(R^{41})(R^{42})$ or adamantyl, or $X^9$ and $X^{10}$ together with $Q^5$ to which they are attached form an optionally substituted 2-phospha-tricyclo[3.3.1.1.{3,7}]decyl group or derivative thereof, or $X^9$ and $X^{10}$ together with $Q^5$ to which they are attached form a ring system of formula 1e;

$Q^1$ and $Q^2$, and $Q^3$, $Q^4$ and $Q^5$ (when present), each independently represent phosphorus, arsenic or antimony;

M represents a Group VIB or VIIIB metal or metal cation thereof;

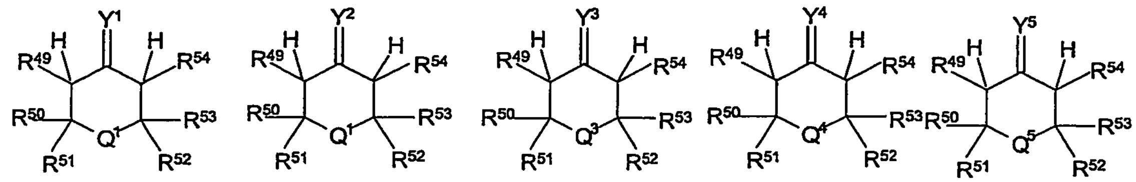
$L_1$ represents an optionally substituted cyclopentadienyl, indenyl or aryl group;

$L_2$ represents one or more ligands each of which are independently selected from hydrogen, lower alkyl, alkylaryl, halo, CO, $P(R^{43})(R^{44})R^{45}$ or $N(R^{46})(R^{47})R^{48}$;

$R^1$ to $R^{18}$ and $R^{31}$ to $R^{42}$, when present, each independently represent lower alkyl, aryl, halo or Het;

$R^{19}$ to $R^{30}$ and $R^{43}$ to $R^{48}$, when present, each independently represent hydrogen, lower alkyl, aryl or Het;

the ring systems of formula 1a, 1b, 1c, 1d and 1e are represented by the formulae



(1a) (1b) (1c) (1d) (1e)

$R^{49}$, $R^{54}$ and $R^{55}$, each independently represent hydrogen, lower alkyl or aryl; $R^{50}$ to $R^{53}$ each independently represent lower alkyl, aryl or Het; and $Y^1$, $Y^2$, $Y^3$, $Y^4$ and $Y^5$, each independently represent oxygen, sulfur or N-$R^{55}$;

n = 0 or 1;

and m = 0 to 5;

provided that when n = 1 then m equals 0, and when n equals 0 then m does not equal 0;

provided that when both K represents $-A_3-Q^3(X^5)X^6$ and E represents $-A_5-Q^5(X^9)X^{10}$, then D represents $-A_4-Q^4(X^7)X^8$.

2. A compound as claimed in claim 1 wherein D and E are identical.

3. A compound as claimed in claim 2 wherein D, E and K are identical.

4. A compound as claimed in any one of the preceding claims wherein K, D and E independently represent $C_1$-$C_6$ alkyl, preferably unsubstituted $C_1$-$C_6$ alkyl, $-CF_3$, or hydrogen, especially hydrogen.

5. A compound as claimed in claim 1 wherein D and E together with the carbon atoms of the cyclopentadienyl

ring to which they are connected form an unsubstituted phenyl ring.

6. A compound as claimed in any one of the preceding claims wherein $X^1$ and $X^2$ represent identical substituents, $X^3$ and $X^4$ represent identical substituents, $X^5$ and $X^6$ (when present) represent identical substituents, $X^7$ and $X^8$ (when present) represent identical substituents, and $X^9$ and $X^{10}$ (when present) represent identical substituents.

7. A compound as claimed in any one of the preceding claims wherein $X^1$ represents $CR^1(R^2)(R^3)$, $X^2$ represents $CR^4(R^5)(R^6)$, $X^3$ represents $CR^7(R^8)(R^9)$ and $X^4$ represents $CR^{10}(R^{11})(R^{12})$, wherein $R^1$ to $R^{18}$ each independently represent $C_1$ to $C_6$ alkyl, $C_1$-$C_6$ alkylphenyl or phenyl, or $R^1$ to $R^3$ together, $R^4$ to $R^6$ together, $R^7$ to $R^9$ together, $R^{10}$ to $R^{12}$ together, $R^1$ and $R^2$ together, $R^4$ and $R^5$ together, $R^7$ and $R^8$ together, $R^{10}$ and $R^{11}$ together independently form a cyclic alkyl group, preferably $R^1$ to $R^{18}$ each independently represent non-substituted $C_1$ to $C_6$ alkyl.

8. A compound as claimed in claim 7 when dependent on claims 1 or 2 wherein K represents $-A_3-Q^3(X^5)X^6$ and $X^5$ represents $CR^{13}(R^{14})(R^{15})$ and $X^6$ represents $CR^{16}(R^{17})(R^{18})$, wherein $R^{13}$ to $R^{18}$ each independently represent $C_1$ to $C_6$ alkyl, $C_1$-$C_6$ alkylphenyl or phenyl, or $R^{13}$ to $R^{15}$ together, $R^{16}$ to $R^{18}$ together, $R^{13}$ and $R^{14}$ together, $R^{16}$ and $R^{17}$ together independently form a cyclic alkyl group, preferably $R^{13}$ to $R^{18}$ each independently represent non-substituted $C_1$ to $C_6$ alkyl.

9. A compound as claimed in claim 7 or 8 wherein D represents $-A_4-Q^4(X^7)X^8$ wherein $X^7$ represents $CR^{31}(R^{32})(R^{33})$

and $X^8$ represents $CR^{34}(R^{35})(R^{36})$, wherein $R^{31}$ to $R^{36}$ each independently represent $C_1$ to $C_6$ alkyl, $C_1$-$C_6$ alkylphenyl or phenyl, $R^{34}$ to $R^{36}$ together, $R^{31}$ to $R^{33}$ together, $R^{31}$ and $R^{32}$ together, $R^{34}$ and $R^{35}$ together independently form a cyclic alkyl group, preferably $R^{31}$ to $R^{36}$ each independently represent non-substituted $C_1$ to $C_6$ alkyl.

10. A compound as claimed in claim 7, 8 or 9 wherein E represents $-A_5$-$Q^5(X^9)X^{10}$ wherein $X^9$ represents $CR^{37}(R^{38})(R^{39})$ and $X^{10}$ represents $CR^{40}(R^{41})(R^{42})$, wherein $R^{37}$ to $R^{42}$ each independently represent $C_1$ to $C_6$ alkyl, $C_1$-$C_6$ alkylphenyl or phenyl, or $R^{37}$ to $R^{39}$ together, $R^{40}$ to $R^{41}$ together, $R^{37}$ and $R^{38}$ together, $R^{40}$ and $R^{41}$ together independently form a cyclic alkyl group, preferably $R^{37}$ to $R^{41}$ each independently represent non-substituted $C_1$ to $C_6$ alkyl.

11. A compound as claimed in any one of claims 1 to 6 wherein $X^1$, $X^2$, $X^3$ and $X^4$ each independently represent an adamantyl group.

12. A compound as claimed in claim 11 when dependent on claims 1 or 2 wherein K represents $-A_3$-$Q^3(X^5)X^6$ wherein $X^5$ and $X^6$ independently represent an adamantyl group.

13. A compound as claimed in claim 11 or 12 wherein D represents $-A_4$-$Q^4(X^7)X^8$ wherein $X^7$ and $X^8$ independently represents an adamantyl group.

14. A compound as claimed in any one of claims 11 to 13 wherein E represents $-A_5$-$Q^5(X^9)X^{10}$ wherein $X^9$ and $X^{10}$ independently represents an adamantyl group.

15. A compound as claimed in any one of claims 1 to 6 wherein $X^1$ and $X^2$ together with $Q^2$ to which they are attached represents 2-phospha-adamantyl and $X^3$ and $X^4$ together with $Q^1$ to which they are attached represents 2-phospha-adamantyl.

16. A compound as claimed in claim 15 when dependent on claims 1 or 2 wherein K represents $-CH_2-Q^3(X^5)X^6$ wherein $X^5$ and $X^6$ together with $Q^3$ to which they are attached represents 2-phospha-adamantyl.

17. A compound as claimed in claim 15 or 16 wherein D represents $-CH_2-Q^4(X^7)X^8$ wherein $X^7$ and $X^8$ together with $Q^4$ to which they are attached represents 2-phospha-adamantyl.

18. A compound as claimed in claim 15, 16 or 17 wherein E represents $-CH_2-Q^5(X^9)X^{10}$ wherein $X^9$ and $X^{10}$ together with $Q^5$ to which they are attached represents 2-phospha-adamantyl.

19 A compound as claimed in any one of claims 1 to 6 wherein $X^1$ and $X^2$ together with $Q^2$ to which they are attached form a ring system of formula Ia, $X^3$ and $X^4$ together with $Q^1$ to which they are attached form a ring system of formula Ib, wherein $Y^1$ and $Y^2$ both represent oxygen.

20. A compound as claimed in claim 19 when dependent on claims 1 or 2 wherein K represents $-CH_2-Q^3(X^5)X^6$ wherein $X^5$ and $X^6$ together with $Q^3$ to which they are attached form a ring system of formula Ic, wherein $Y^3$ represents oxygen.

21. A compound as claimed in claim 19 or 20 wherein D represents $-CH_2-Q^4(X^7)X^8$ wherein $X^7$ and $X^8$ together with $Q^4$

to which they are attached form a ring system of formula Ic, wherein $Y^3$ represents oxygen.

22. A compound as claimed in claim 19, 20 or 21 wherein E represents $-CH_2-Q^5(X^9)X^{10}$ wherein $X^9$ and $X^{10}$ together with $Q^5$ to which they are attached form a ring system of formula Ie, wherein $Y^5$ represents oxygen.

23. A compound as claimed in any one of claims 7, 8, 11, 12, 15, 16, 19 or 20 wherein D and E together with the carbon atoms of the cyclopentadienyl ring to which they are attached form an unsubstituted phenyl ring.

24. A compound as claimed in any one of the preceding claims wherein each of $Q^1$ and $Q^2$, and $Q^3$, $Q^4$ and $Q^5$, (when present), are the same, preferably phosphorus.

25. A compound as claimed in any one of the preceding claims obtainable by combining: (a) palladium or a compound thereof; and (b) a compound of formula I.

26. A compound as claimed in anyone of the preceding claims wherein $A_1$ and $A_2$, and $A_3$, $A_4$ and $A_5$ (when present), each independently represent $C_1$ to $C_6$ alkylene.

27. A compound as claimed in anyone of the preceding claims wherein each of $A_1$ and $A_2$, and $A_3$, $A_4$ and $A_5$ (when present), are identical and represent $C_1$ to $C_6$ alkylene, preferably methylene.

28. A compound as claimed in anyone of the preceding claims wherein M in a compound of formula I represents Cr, Fe, Co, Mo or Ru or a metal cation thereof.

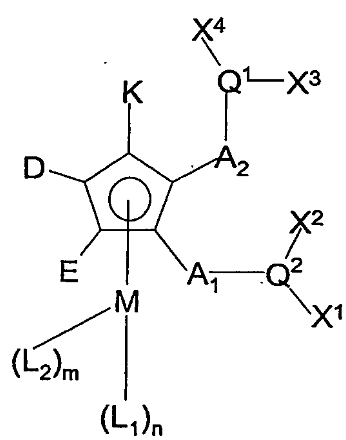
29. A compound as claimed in claim 28 wherein M represents iron or a cation thereof.

30. A compound as claimed in anyone of the preceding claims wherein wherein n=1, m=0 $L_1$ represents cyclopentadienyl, indenyl, phenyl or napthyl, preferably unsubstituted cyclopentadienyl.

31. A compound as claimed in anyone of claims 1 to 29 wherein n = 0 and m = 3 or 4, preferably 3, and $L_2$ represents one or more ligands each of which ligands are independently selected from $C_1$ to $C_4$ alkyl, chloro, CO, $PR^{43}R^{44}R^{45}$ or $NR^{46}R^{47}R^{48}$.

32. A process for preparing a compound as defined in any one of claims 1 to 31 comprising combining (a) a Group VIIIB metal or compound thereof; and, (b) a compound of formula I as defined in any one of claims 1 to 30.

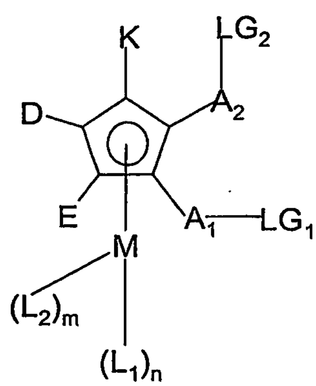
33. A compound of formula I




(I)

wherein $A_1$, $A_2$, K, D, E, M, $L_2$, $L_1$, $Q^1$, $Q^2$, $X^1$, $X^2$, $X^3$, $X^4$, n and m are as defined in any one of claims 1 to 31.

34. A process for preparing a compound of formula I as defined in claim 33, comprising reacting a compound of formula II wherein $A_1$, $A_2$, K, D, E, M, $L_1$, $L_2$, n and m are as defined for a compound of formula I, and $LG_1$ and $LG_2$ represent suitable leaving groups, with a compound of formula IIIa and IIIb



(II)

$HQ^2(X^1)X^2$

(IIIa)

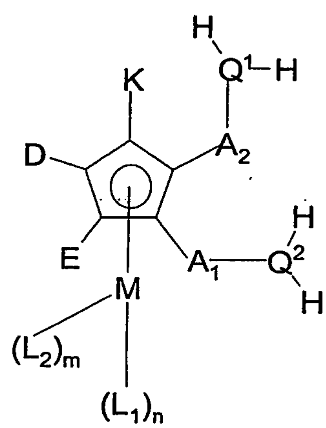
$HQ^1(X^3)X^4$

(IIIb)

wherein $X^1$, $X^2$, $Q^2$, $X^3$, $X^4$ and $Q^1$ are as defined in anyone of claims 1 to 31.

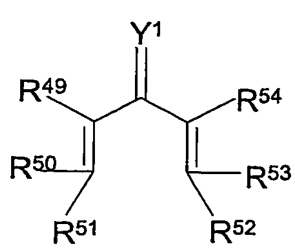
35. A compound of formula II as defined in claim 34.

36. A process for preparing a compound of formula I wherein K, D, E, M, $A_2$, $A_1$, $L_2$, $L_1$, $Q^1$, $Q^2$, m and n are as defined in any one of claims 1 to 31 and $X^1$ and $X^2$ together with $Q^2$ to which they are attached form a ring system of formula Ia as defined in anyone of claims 1 to 31 and $X^3$ and $X^4$ together with $Q^1$ to which they are attached form a ring system of formula Ib as defined in any one of claims 1 to 31, comprising reacting a compound of formula XV

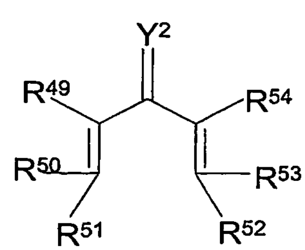


(XV)

wherein K, D, E, M, $A_2$, $A_1$, $L_2$, $L_1$, $Q^1$, $Q^2$, m and n are as defined in any one of claims 1 to 31, with a compound of formula XVIa and XVIb



(XVIa)



(XVIb)

wherein $Y^1$, $Y^2$, $R^{49}$ to $R^{55}$ are as defined for a compound of formula I.

37. A compound of formula XV as defined in claim 36.

38. A process for the carbonylation of an ethylenically unsaturated compound comprising contacting an ethylenically unsaturated compound with carbon monoxide and a co-reactant in the presence of a compound as defined in any one of claims 1 to 31.

39. A process as defined in claim 37 wherein the co-reactant includes a hydroxyl group containing compound.

40. A process as claimed in claim 37 or 38 wherein the ethylenically unsaturated compound comprises ethylene.

41. A process as claimed in any one of claims 38 to 40, further including the step of including a source of anions.

42. A composition comprising a compound as defined in any one of claims 1 to 31 attached to a support.

43. Use of a compound as defined in anyone of claims 1 to 31 or a composition as defined in claim 40 as a catalyst.

## ABSTRACT

A catalyst suitable for carbonylating ethylenically unsaturated compounds comprising a Group VIIIB metal or compound thereof and a metallocene.